

5.5 INDICATOR ~~CHEMICALS CONTAMINANTS~~ IN TRANSITION ZONE WATER AND GROUNDWATER SEEPS

This section summarizes the Study Area data for TZW and groundwater seeps. As described in [Section 3](#), the transition zone is defined as the interval where both groundwater and surface water comprise some percentage of the water occupying pore space in the sediments. The primary focus ~~area~~ of the transition zone for this investigation is [within the surface sediment mixed layer, which is considered to be the upper 30 cm of the shallow sediment \(0 to 38 cm bml\), and which includes the biologically active zone.](#)¹ ~~The mixed layer is characterized by TZW samples collected in the shallow (0 to 38 cm bml) sediments.~~ Deeper (>90 cm bml) TZW samples are also discussed here to lend insight into observed chemical distribution patterns ~~and to support an assessment of potential TZW loading impacts to surface water and surface sediment that is provided in Appendix E and Section 6.1.6.~~

The following subsections present tables, plan view maps, ~~with~~ histograms, ~~and~~ scatter plots, ~~and stacked bar charts~~, to support brief discussions of nature and extent for the select IC list (Table 5.10-2). The full RI data sets for TZW and groundwater seeps for all sampled chemicals (those data of adequate quality ~~for use in decision making for the Study Area per the Portland Harbor RI/FS Programmatic Work Plan [Integral et al. 2004]~~) are presented in the ~~project RI~~ SCRA database ([Appendix A3](#)) and summarized in [Appendix D4](#), Tables D4-1 and D4-2. [In addition, TZW sampling results are compared to various water screening values in \[Appendix D3.3\]\(#\).](#)

5.5.1 Transition Zone Water

The TZW sampling effort was ~~not a harbor-wide study of TZW, but instead was a focused investigation offshore of nine study sites. It is likely possible that there are~~ ~~Other areas of groundwater plume discharge to the river not captured in this data set.~~ Further, the sampling investigation of TZW did not seek to delineate areas impacted by ~~upland sourced groundwater plumes or impacted by river sediments.~~²

The TZW investigations performed for the RI focused solely on areas of confirmed or likely groundwater ~~plume~~ discharge to the river and did not seek to characterize pore water chemistry elsewhere in the Study Area. Accordingly, this discussion does not address TZW/pore water chemistry in areas with no upland groundwater discharge, or areas of clean groundwater flowing through contaminated sediments. Additionally, this

¹ The surface sediment mixed layer depth is based on analysis of bathymetric data, as discussed in Section 2, which indicates that processes disturb or mix sediments from >20 to 30 cm bml in some areas of the Study Area. The biologically active zone is defined by the depth of biological processes. The depth of the true biologically active zone varies widely throughout the Study Area, based on factors that control benthic community structure, such as sediment texture, sediment-water interface dynamics, and organic loading.

² In areas not directly affected by transport of ~~chemical~~ contaminants originating in upland groundwater, ~~chemical~~ contaminants may be present in TZW as a result of desorption from contaminated sediments and/or geochemical processes within the sediments and associated TZW.

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study does not distinguish the relative contribution of upland groundwater discharges to surface water plumes and chemical contaminants in sediment to the concentrations measured in TZW.

TZW data for ICs are presented on plan-view maps and/or scatter plots, as well as stacked bar charts for select chemical contaminants to support evaluation of sample composition. These presentations vary by analyte and the data are summarized in Table 5.45-1. As reflected in Table 5.45-1, the TZW analyte lists varied by study site; therefore, it was often unnecessary to produce maps for each river mile for a given analyte.

Maps: Map presentations of TZW data use color-coded symbols and fly out labels to provide the individual concentration values. This presentation includes distinction of Peeper samples (0 to 38 cm bml), shallow TZW Trident samples (0 to 380 cm bml) and deeper Trident samples (90 to 150 cm bml), as well as non-LWG shallow (0 to 90 cm bml)³ and deeper (91 cm bml) Geoprobe samples. Paired map sets are presented for each river mile to show filtered and unfiltered results, where available. Semi permeable membrane devices (pPeeper) samples are presented with a unique symbol on both filtered and unfiltered images to allow for a detailed evaluation of results. A histogram of detected chemical contaminant concentrations is inset on each map to provide context for the results presented on the given river mile relative to the results from the entire Study Area. Histogram bins and concentration color ranges were selected based on professional judgment to best present the complete range of filtered and unfiltered concentration values observed across the Study Area. -Maps 5.5-1 through 5.5-6 are provided for major ICs, including Total DDx, Total PAHs, arsenic, chromium, copper and zinc.

Scatter Plots: Scatter-plot presentations of TZW data show sample concentrations plotted according to the river mile of the sample location. Color-coded symbols distinguish sample type and depth. Paired plot sets are presented for each chemical contaminant to show filtered and unfiltered results, where available. Peeper samples are presented with a unique symbol on both filtered and unfiltered images to allow for a detailed evaluation of results. Scatter plots are provided for Total DDx, Total PAHs, arsenic, chromium, copper and zinc as Figures 5.5-1a-f.

Bar Charts: Stacked bar charts of total DDx, total PAHs, and TPH present, for each individual TZW sample, the fractional contribution of each individual constituent of the total concentration (detected sums only). The total sum concentration is also denoted on the figure with a black line (scale on the right hand y axis). Samples are organized along the x axis according to descending river mile order, grouped by understanding of

³ For the Gasco study (sample IDs that begin with "GS-"), the sample collected at the uppermost depth in the 0 to 90 cm bml interval at each location is presented on maps as the best available representation of the TZW concentrations in the shallow layer. No deeper data collected as part of the Gasco study is presented. For the Siltronic study (sample IDs that begin with "GP-"), samples collected at 31 cm bml are presented as shallow TZW, and samples collected at 91 cm bml are presented as deeper TZW.

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~~groundwater discharge areas as discussed in detail in Appendix C2. Where available, peeper ("PR"), filtered and unfiltered Trident ("TR"), and Geoprobe ("GP") data are shown for each sample location. Sample IDs for filtered results ("F" in the sample ID) are indicated by highlighting. Deeper Trident samples are denoted by "90", "120", or "150" in the sample ID, referring to depth bml in centimeters. Further, field duplicate samples on these figures are denoted by "dup" in the sample ID.~~

The TZW presentation provided in [this section](#) ~~Section 5.4~~ supports the detailed site-by-site presentation and analysis of groundwater pathways presented in Appendix C2. The Appendix C2 presentation of TZW provides data analysis focused on identification of complete groundwater pathways from upland plumes to the transition zone, including some cross-media analysis. This section ~~(Section 5.4)~~ focuses on presentation of the distribution of ICs observed in the transition zone. As such, this section does not ~~attempt to present cross-media analysis or to relate observations to sources~~ [discuss all contaminants from groundwater sources within the Study Area](#). ~~Due to the spatially focused nature of the TZW and seep sampling programs, this discussion of nature and extent includes use of facility names for location reference; mention of facility names does not necessarily indicate source origin.⁴ The findings presented in Appendix C2 and in this nature and extent discussion are incorporated into the detailed cross-media analysis and sources discussions presented in the Study Area-wide CSM discussion (Section 10).~~

This section is organized somewhat differently than the *In-River Distribution* discussions for other media. Specifically, this TZW section includes presentation of all TZW ICs in the main report, which is unlike the discussion format used for other media such as sediment (Section 5.1) and surface water (Section 5.3). This difference reflects the lists of chemicals that were the focus of the various upland site-specific TZW investigations. In particular, PCBs were not sampled in TZW,⁵ and only two TZW sampling locations were analyzed for PCDD/Fs.⁶ Neither PCBs nor PCDD/Fs are expected to be migrating to the river via groundwater given their high hydrophobicity and the lack of evidence of facilitated transport at upland sites with these COIs. Because of the unique TZW IC list and the complexities of the groundwater pathway, discussion of all TZW ICs is needed for a meaningful presentation of the in-river distribution of TZW results. Because all TZW ICs are discussed in the main text, a paired summary statistics table of a subset of ICs is not provided in the main text, as is done for other media. [Instead, all summary statistics are presented in Appendix D4 \(Tables D4-1 and D4-2\).](#)

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⁴ The TZW sampling effort was a focused investigation offshore of nine upland sites and was not a harbor-wide study. The approach taken for selection of TZW study sites is presented in Appendix C2. It is possible that other sites will be identified that have a complete pathway for upland groundwater plumes to the Study Area.

⁵ PCBs were not identified as COIs for any of the nine TZW sites. PCB data were not collected in TZW and are not discussed here.

⁶ PCDD/Fs were detected in only one TZW sample: Trident-filtered (0.865 pg/L) and unfiltered (29 pg/L) at station RP-07-B.

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5.5.25.5.1.1 TZW Data Set

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This subsection describes the TZW chemistry data set presented in this RI Report. The TZW chemistry data used in this investigation were generated during the following field events (sampling locations are shown on Map 2.2-6):

2004 Pilot Study – In 2004, a pilot study was conducted offshore of the Arkema and ARCO sites to evaluate various TZW sampling methods, including Trident® push probe, small volume peepers, large volume peepers, bulk sediment centrifugation, Geoprobe®, and vapor diffusion samplers. The findings of the 2004 Pilot Study are discussed in detail in Appendix B of the GWPA Sampling and Analysis Plan (SAP; Integral 2005e), the Discharge Mapping FSP (Integral 2005b), and the TZW FSP (Integral 2006a). The pilot study found that TZW samples collected by Trident push probe and small volume peepers provided the most accurate and reproducible results for the targeted zones and sediment conditions encountered.⁷ Based on those findings, only those tools were applied to subsequent LWG investigations. The 2004 Pilot Study results included in the RI TZW data set consist of results for only the 10 Trident push probe and 9 small volume peeper locations sampled offshore of the ARCO and Arkema sites (data collected by other evaluated methods are not included). Included Pilot Study samples were collected in the shallow sediment interval at 30 cm bml (Trident) and from 0 to 38 cm bml (peeper).

2005 Round 2 GWPA – Between August and December 2005, the LWG conducted an investigation of TZW offshore of nine upland sites with known or likely pathways for groundwater plume transport of chemicals to the river. Site selection is discussed further in Section 5.4.1.1 (below) and in Appendix C2. Fifty six Trident and 27 small volume peeper locations were sampled as part of this investigation, and all of those results are included here. Trident samples were collected in the shallow sediment interval at 30 cm bml at all 56 sample locations, as well as in deeper sediment (90, 120, or 150 cm bml) at 23 of these locations. Peeper samples were collected in the shallow sediment interval, from 0 to 38 cm bml, at all 27 peeper sample locations. The sampling program is described in detail in the TZW FSR (Integral 2006d), and the findings related to groundwater pathways are discussed in detail in Appendix C2.

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2005 Siltronic Investigation – In 2004 and 2005, on behalf of Siltronic, Maul Foster & Alongi (MFA) conducted an investigation of the groundwater pathway offshore of the Siltronic site. These data are presented in detail by MFA (HAI 2005b; MFA 2005b), and discussed in Appendix C2. The results of the 2004 and 2005 investigations indicate areas of groundwater discharge in a subset of the area investigated (MFA 2007). Additional results of these studies are presented in Appendix C2. The TZW samples

⁷ The Round 2 GWPA TZW-SCSR (Integral 2006e) presents detailed information regarding the quality of the Round 2 TZW data set developed and analyzed as part of the Round 2 GWPA. These data meet project specific data quality objectives specified in the SAP (Integral 2005e) and QAPP (Integral 2005a), and statistical analysis of sample replicates shows excellent overall reproducibility of sample results, with both small volume peepers and Trident samples comparing well. These findings support a high level of confidence in both the analytical data sets and the methods and equipment used for sample collection.

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were collected with a Geoprobe sampler, which can be used as a push probe type of sampling tool for TZW. Forty one TZW samples collected in the shallow sediment interval at 31 cm bml, as well as 24 samples collected in a deeper interval at 91 cm bml, are included in this presentation of TZW nature and extent.

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2007 Gasco Investigation – In 2007, on behalf of Gasco, Anchor Environmental conducted an investigation of the groundwater pathway offshore of the Gasco site. These data are presented in detail in Anchor (2008b) and discussed in Appendix C2. TZW samples were collected with a Geoprobe sampler. Twenty two TZW samples collected between 0 and 90 cm bml are included in this presentation of TZW nature and extent. Note that very few samples were collected in the shallow (0 to 38 cm bml) sediment interval for this Gasco investigation. Therefore, the sample collected at the uppermost depth at each location is used in this nature and extent discussion as the best available representation of the TZW concentrations in the shallow layer. No deeper data collected as part of the Gasco Investigation was included in this nature and extent discussion.⁸

5.5.2.1 Study Sites

These sampling activities described above focused on the offshore area of nine sites along the west bank of the river (see Map 2.12-206):

- Kinder Morgan Linnton Terminal (RM 4.1 to RM 4.2)
- ARCO Terminal 22T (RM 4.7 to RM 4.9)
- ExxonMobil Oil Terminal (RM 4.8 to RM 5.1)
- Gasco (RM 6.1 to RM 6.5)
- Siltronic (RM 6.3 to RM 6.5)
- Rhone Poulenc (RM 6.7 to RM 6.9)
- Arkema (Acid Plant and Chlorate Plant areas; RM 7.2 to RM 7.5)
- Willbridge Terminal (RM 7.6 to RM 7.8)
- Gunderson (RM 8.3 to RM 8.5).

These nine sites were identified for investigation as part of the Round 2 GWPA as high priority Category A upland groundwater sites, selected in agreement with EPA as sites with a confirmed or reasonable likelihood for discharge of COIs to Portland Harbor.⁹ The approach to site selection is discussed in greater detail in Appendix C2.

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⁸ Only one sample (GS-C2, 73 to 103 cm bml) in the 2007 Gasco Investigation was collected in the deeper (90 to 150 cm bml) sample interval; this sample is not included in this nature and extent discussion.

⁹ Site selection criteria included: (1) Existing offshore groundwater sampling data indicate that a potentially complete transport pathway exists for groundwater COIs to reach the transition zone; (2) Existing shoreline sampling data from groundwater wells or seeps indicate a reasonable likelihood of a complete transport pathway for groundwater COIs to reach in river exposure points; (3) Existing observations of NAPL seepage to the river

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TZW sampling offshore of each site was focused largely on the in-river areas adjacent to the site shoreline, often extending to, and occasionally just beyond, the navigation channel boundary. As such, the TZW sampling effort was not a harbor-wide study of TZW, but instead was a focused investigation offshore of the nine Round 2 study sites. (Note: non-LWG TZW investigations offshore of the Siltronic and Gasco sites are considered with the LWG Round 2 GWPA results, as discussed in Section 5.4.1 above.) It is possible that there are other areas of groundwater plume discharge to the river not captured in this data set.

The TZW investigations performed for the RI focused solely on areas of confirmed or likely groundwater plume discharge to the river and did not seek to characterize pore water chemistry elsewhere in the Study Area. Accordingly, this discussion does not address TZW pore water chemistry in areas with no upland groundwater discharge, or areas of clean groundwater flowing through contaminated sediments. Additionally, this study does not distinguish the relative contribution of upland groundwater plumes and chemicals in sediment to the concentrations measured in TZW. Consideration of pore water chemistry affected by in-river sediment contamination is evaluated in Section 6 loading calculations through equilibrium partitioning calculations based on the large data set of sediment concentrations. These calculated estimates of pore water concentrations are not presented here as part of the TZW nature and extent presentation because they are not actual field measurements.

5.5.2.2 Sampling Techniques

Two general types of sampling techniques were used to collect the TZW samples: small volume peepers and push probe samplers (Trident and Geoprobe¹⁰ tools were used as push probe samplers). These are described in detail in the Pilot Study FSP (Integral 2004a). The Round 2 TZW investigation used both Trident and small volume peepers, and the non-LWG investigations at Gasco and Siltronic used Geoprobe to collect TZW samples.

For the Round 2 TZW investigation, paired unfiltered and filtered samples were collected with the Trident tool, where possible. At these locations, collection of unfiltered samples was given priority, and volume limitations prevented collection of filtered samples in some cases. Filtered samples were not collected for small volume peeper samples from the Round 2 TZW investigation due to volume limitations and the across-membrane equilibration nature of the sampling technique,¹¹ which was expected

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indicate that a complete transport pathway may exist for groundwater COIs to reach in-river exposure points; and (4) Shoreline groundwater seeps containing COIs are known to be present and represent a potentially complete exposure pathway for human receptors.

¹⁰ Geoprobe sampling of TZW was performed by Siltronic and Gasco. The data are included in the SCRA project database as non-LWG collected data.

¹¹ Note that the peeper is a diffusion-based sampling device, and water samples captured in the peeper device must pass through a 5-µm Teflon[®] membrane. Therefore, peeper samples are not whole water samples, yet these samples do include particles larger than the 0.45-µm diameter filter used for Trident filtered samples.

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to introduce fewer solids than peristaltic pumping for push probe samples. Filtered Geoprobe samples were collected as part of the Anchor (2008b) investigation at Gasco for metals and PAHs only. No filtered Geoprobe samples were collected by MFA as part of the Siltronic investigation (MFA 2005b).

All peeper samples were collected over the depth interval of 0 to 38 cm bml. Trident samples were collected at 30 cm bml, with a few deeper samples collected between 90 and 150 cm bml.¹² Geoprobe samples were collected at depths ranging from 30 to 6,300 cm bml, though only Geoprobe samples from 0 to 91 cm bml are presented in this discussion of TZW nature and extent. The nature and extent presentation focus on the shallow (0 to 38 cm bml) TZW data corresponds to the surface sediment mixed layer (≤ 30 cm bml). Deeper Trident and Geoprobe TZW sample data (90 to 150 cm bml) are presented here to advance the understanding of the completeness of specific groundwater pathways, and are discussed in more detail in Appendix C2.

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5.5.2.3 Spatial and Temporal Representativeness of the TZW Data Set

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TZW sampling was limited to the offshore areas of the nine study sites as described above. As noted above, there may be additional upland plumes for which delineation was not adequate enough to have been categorized as having a confirmed or likely pathway to the river (upland site plume delineation is outside of the LWG investigation responsibility). Further, the sampling investigation of TZW did not seek to delineate TZW chemistry in areas unimpacted by upland plumes but possibly impacted by river sediments.¹³

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Because TZW samples were collected at a single point in time (for Trident and Geoprobe sampling) or over a 3-week equilibration period (for peeper sampling), LWG field sampling events were carefully timed to maximize the expected upland groundwater signal (i.e., the time of greatest groundwater discharge rate). For the Pilot Study and Round 2 TZW investigations, TZW analytical samples were collected from November 2004 to January 2005 and October to December 2005, respectively, before river water levels increased to the higher levels that typically occur from mid-winter through spring. The non-LWG TZW samples collected at Gasco that are included in this nature and extent discussion were collected between July and September 2007. The non-LWG TZW samples collected at Siltronic that are discussed here were collected in May and June of 2005.

~~Daily tidal fluctuations are not expected to have affected the representativeness of the analytical chemistry results collected by either small volume peepers or the push probe samplers. First, small volume peepers were left in place over 3 weeks, allowing~~

¹² One Trident sample was collected at 60 cm bml at location CP-07-B. This sample is included with the 90 to 150 cm bml data set.

¹³ In areas not directly affected by transport of chemicals originating in upland groundwater, chemicals may be present in TZW as a result of desorption from contaminated sediments and/or geochemical processes within the sediments and associated TZW.

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equilibration over many tidal cycles. Second, seepage meter results (presented and discussed in Appendix C2) suggest that Trident samples from depths of 30 cm bml or deeper are unlikely to be affected by tidal changes in the areas sampled. The typical discharge rate measured by seepage meters was on the order of a few cm/day (average = 1.40 cm/day; minimum daily average = -18.9 cm/day; maximum daily average = 14.2 cm/day). The largest net negative recharge rate¹⁴ among seepage meter locations showing an average positive discharge (i.e., locations where the tidal influence could potentially have a significant timing impact on TZW chemistry) was observed offshore of the Siltronic site. At this location, the negative recharge period covered roughly 9.5 hours, with an average seepage rate of -6.7 cm/day during this period. This corresponds to a net seepage flux of 2.65 cm over the 9.5 hour tidal recharge period. Assuming sediment porosity of 25 percent, the maximum depth of influence for this period of negative seepage would be roughly 10.6 cm before the direction reverses to positive discharge with the tidal change. At this location with the greatest period and magnitude of negative flux (among all locations with net positive flux), this estimated periodic depth of influence of surface water is still well above the minimum sampling depth of 30 cm bml. Therefore, the timing of tidal conditions during Trident sample collection is not expected to have had any effect on chemistry results.¹⁵

5.5.1.2 Total PCBs in TZW

PCB data were not collected in TZW samples collected from the offshore areas of nine sites along the west bank of the river were not analyzed for PCBs at any of the nine locations where measurements were taken.

5.5.1.3 Total PCDD/Fs in TZW

Only two TZW sampling locations were collected using Trident sampling methodology from two locations adjacent to Rhone Poulenc for ~~were analyzed for PCDD/Fs analyses~~; RP-03-C and Rhone Poulenc (RP-07-B) and ~~where? PCDD/Fs were detected in only one TZW sample: Trident filtered (0.865 pg/L) and unfiltered (29 pg/L) at Rhone Poulenc station RP-07-B. Sample RP-03-C was collected from a depth of 0 to 30 cm bml and analyzed for filtered and unfiltered PCDD/Fs, which were not detected above laboratory reporting limits. A parent and duplicate sample were collected from RP-07-B from a depth of 0 to 30 cm bml for filtered and unfiltered PCDD/F analyses. PCDD/Fs were detected in the parent and duplicate unfiltered samples, with concentrations of 29 pg/L to 51.3 pg/L, respectively. PCDD/Fs were only detected in the parent filtered sample, with a concentration of 0.865 pg/L.~~

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¹⁴ The negative seepage rate values are the focus here because they correspond to observed recharge to the TZW from surface water, which is the concern related to tidal influence on the timing of TZW sampling.

¹⁵ These calculations are further supported by a temporal tidal study conducted offshore of the Gasco and Siltronic sites as part of the Anchor 2007 investigation. That investigation involved collection of 30 TZW samples from three mini-piezometers (~45 cm bml) over multiple tidal cycles and concluded that there were no correlations with river stage for any of the COIs analyzed.

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5.5.1.4 -TCDD TEQ

As described above, samples were collected using Trident sampling methodology from two locations adjacent to Rhone Poulenc for PCDD/Fs analysis, RP-03-C and RP-07-B-TR. Total TEQs were calculated for the detected results in the parent and duplicate unfiltered samples collected from RP-07-B. The calculated concentrations were 1.72 J pg/L and 1.32 J pg/L, respectively.

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5.5.3 Indicator Chemical List for TZW

The IC list for TZW is presented in Table 5.0-2. A total of 39 individual analytes and calculated sums (total cPAHs, total HPAHs, and total PAHs; total DDE, total DDD, total DDT, and total DDX; total xylenes) were identified as ICs for TZW in consultation with EPA (see Section 5.0). These chemicals were selected from the complete list of TZW sampled analytes, taking into consideration the subset of chemicals found to be relevant through the human health and ecological risk screening process, the chemicals identified for detailed assessment in the CSM discussion in Section 10, as well as any additional chemicals which were the focus of the Round 2 TZW investigation. The resulting list of chemicals can be placed into seven groups, as follows (chemicals included in the Section 10 CSM discussion are denoted with an asterisk [*]):

- PAHs

- Total PAHs*

- Total LPAHs¹⁶

- Total HPAHs

- Total cPAHs¹⁴

- Total cPAHs BaPEq values

- BAP

- Naphthalene

- TPH¹⁷

- TPH-DRH

- TPH-RRH

- TPH-Gasoline-range hydrocarbons (GRH)

- Metals

- Arsenic*

- Barium

- Cadmium

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¹⁶ LPAHs and cPAHs are discussed here to provide for complete discussion of total PAHs and HPAHs though they are not included in the indicator chemical list for TZW.

¹⁷ TPH is not on the TZW indicator chemical list; however, it is presented in this section to support discussion of DRH, RRH, and GRH.

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- ~~—Copper*~~
- ~~—Lead~~
- ~~—Manganese~~
- ~~—Nickel~~
- ~~—Zinc*~~
- ◆ **Pesticides**
- ~~—Total DDx (2,4'- and 4,4'-DDD, DDE, DDT)*~~
- ~~—Total of 2,4'- and 4,4'-DDT~~
- ~~—Total of 2,4'- and 4,4'-DDE~~
- ~~—Total of 2,4'- and 4,4'-DDD~~
- ◆ **Herbicides**
- ~~—2,4,5-TP (Silvex®)~~
- ◆ **VOCs**
- ~~—Monochlorobenzene (MCB)~~
- ~~—1,2-Dichlorobenzene (1,2-DCB)~~
- ~~—1,2,4-Trimethylbenzene~~
- ~~—Chloroethane~~
- ~~—1,2-Dichloroethane (1,2-DCA)~~
- ~~—1,1,2-Trichloroethane (1,1,2-TCA)~~
- ~~—Vinyl chloride~~
- ~~—cis-1,2-Dichloroethene (cis-1,2-DCE)~~
- ~~—Trichloroethene (TCE)~~
- ~~—Chloroform~~
- ~~—Methylene chloride~~
- ~~—Carbon disulfide~~
- ~~—Total BTEX (including individual component chemicals)~~
- ◆ **Other**
- ~~—Perchlorate~~
- ~~—Cyanide.~~

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- Five chemicals (total PAHs, total DDX, arsenic, copper, zinc) included on the TZW IC list are presented in the cross-media analysis of results in Section 10. The following sections present detailed discussions of results for two of these ICs (DDX and PAHs), followed by summary discussions and figures for the remaining ICs on the TZW list.
- In addition, TZW sampling results are compared to various water screening values in Appendix D3.3. Contaminants that exceed one or more screening values are identified and will be included in the contaminant mobility evaluation in the draft FS. Contaminants that pose potential risk to humans are discussed in the BHHRA (Appendix F).

5.5.52 Description of TZW Presentation Tools

- TZW data for TZW ICs are presented on plan-view maps and/or scatter plots, as well as stacked bar charts for select chemicals to support evaluation of sample composition. These presentations vary by analyte and are summarized in Table 5.4-1. As reflected in Table 5.4-1, the TZW analyte lists varied by study site; therefore, it was often unnecessary to produce maps for each river mile for a given analyte. All maps, scatter plots, and bar charts were generated with consistent approaches as described below.
- Maps: Map presentations of TZW data use color-coded symbols and flyout labels to provide the individual concentration values. This presentation includes distinction of shallow TZW Trident samples (0 to 38 cm bml) and deeper Trident samples (90 to 150 cm bml), as well as non-LWG shallow (0 to 90 cm bml)¹⁸ and deeper (91 cm bml) Geoprobe samples. Paired map sets are presented for each river mile to show filtered and unfiltered results, where available. Peeper samples are presented with a unique symbol on both filtered and unfiltered images to allow for a detailed evaluation of results. A histogram of detected chemical concentrations is inset on each map to provide context for the results presented on the given river mile relative to the results from the entire Study Area. Histogram bins and concentration color ranges were selected based on professional judgment to best present the complete range of filtered and unfiltered concentration values observed across the Study Area.

¹⁸ For the Gasco study (sample IDs that begin with "GS"), the sample collected at the uppermost depth in the 0 to 90 cm bml interval at each location is presented on maps as the best available representation of the TZW concentrations in the shallow layer. No deeper data collected as part of the Gasco study is presented. For the Siltronic study (sample IDs that begin with "GP"), samples collected at 31 cm bml are presented as shallow TZW, and samples collected at 91 cm bml are presented as deeper TZW.

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- ~~– Scatter Plots: Scatter-plot presentations of TZW data show sample concentrations plotted according to the river mile of the sample location. Color-coded symbols distinguish sample type and depth. Paired plot sets are presented for each chemical to show filtered and unfiltered results, where available. Peeper samples are presented with a unique symbol on both filtered *and* unfiltered images to allow for a detailed evaluation of results.~~
- ~~– Bar Charts: Stacked bar charts of total DDx, total PAHs, and TPH present, for each individual TZW sample, the fractional contribution of each individual constituent of the total concentration (detected sums only). The total sum concentration is also denoted on the figure with a black line (scale on the right-hand y-axis). Samples are organized along the x-axis according to descending river mile order, grouped by understanding of groundwater discharge areas as discussed in detail in Appendix G2. Where available, peeper (“PR”), filtered and unfiltered Trident (“TR”), and Geoprobe (“GP”) data are shown for each sample location. Sample IDs for filtered results (“f” in the sample ID) are indicated by highlighting. Deeper Trident samples are denoted by “90”, “120”, or “150” in the sample ID, referring to depth bml in centimeters. Further, field duplicate samples on these figures are denoted by “dup” in the sample ID.~~

5.5.575.5.1.5 **Total DDx in TZW**

The following subsections present the in-river distribution of DDx results in TZW samples. The TZW IC-list includes total DDx, total DDD, total DDE, and total DDT. This presentation also discusses the individual DDx components (2,4’ DDE, 4,4’ DDE, 2,4’ DDD, 4,4’ DDD, 2,4’ DDT, and 4,4’ DDT).

5.5.57.1 **Observed Chemical Distribution of DDx in TZW**

DDx components were identified as upland groundwater COIs at the sampled offshore of the former Arkema Acid Plant and Rhone Poulenc area of the Arkema sites in the Round 2 GWPA SAP (Integral et al. 2005). ~~Ten locations offshore of All but two of the samples were collected from locations offshore of the this area Arkema Acid Plant site, and one location (RP-03-C) offshore of the Rhone Poulenc site were analyzed for DDx pesticides in TZW as part of the Round 2 GWPA sampling effort. Additionally, one sample collected offshore of the adjacent Rhone Poulenc site¹⁹ (RP-03-C) was analyzed for DDx pesticides. As shown in Table 5.5-1, there are:~~

- ~~six 8 peeper~~ Peeper samples (0 to 38 cm bml), including two duplicates, collected offshore of the Arkema site;

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¹⁹ DDx was not included on the COI list for the Rhone Poulenc site for the GWPA sampling because pesticides were not expected to be mobile in groundwater at the site (Integral et al. 2005). Subsequent to completion of the GWPA site categorization process, DDx was detected in groundwater at the site (AMEC 2006).

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- 14-18 shallow (0 to 38-30 cm bml) Trident samples, including four duplicates, collected offshore of the Arkema site and Rhone Poulenc (RP-03-C) (with collocated filtered and unfiltered samples collected at six locations); ~~and three~~
- 4 deep (90 to 150 cm bml) Trident samples in this data set (with collocated filtered and unfiltered samples collected at one location), including one sample collected from offshore of the Rhone Poulenc site (RP-03-C).

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~~Total DDx compounds were~~ detected in two of the Peeper samples, with concentrations of 0.032 J ug/L at AP03B-1 and 0.0135 J ug/L at AP04D. DDx compounds ~~were~~ detected in each of the shallow Trident unfiltered samples with concentrations ranging from 0.0075 J ug/L at AP04D to 3.05 J ug/L at AP-03-A. DDx compounds ~~were~~ detected in all but three of the shallow Trident filtered samples with detected concentrations ranging from 0.0084 J ug/L at AP03B-1 to 0.158 NJ ug/L at RP-03-C. DDx compounds ~~were~~ detected in all three of the deep Trident unfiltered samples collected offshore of the Arkema site (0.169 J ug/L to 5.73 J ug/L) and the one offshore of Rhone Poulenc (0.17 J ug/L). DDx compounds ~~were~~ also detected in the unfiltered sample collected offshore of Rhone Poulenc (0.179 J ug/L).

Map 5.45-1 presents filtered (top panel) and unfiltered (bottom panel) total DDx (and constituent sums 2,4'- and 4,4'-DDD, 2,4'- and 4,4'-DDE, 2,4'- and 4,4'-DDT)²⁰ concentrations measured in shallow (0 to 38-30 cm bml) Trident and deep (90 to 150 cm bml) Trident samples. Peeper samples are presented with a unique symbol on both filtered and unfiltered images to allow for a detailed evaluation of results. Inset histograms on Map 5.45-1 show the distribution of total DDx sample concentrations for detected filtered, unfiltered, and ~~peeper-peeper~~ results. Scatter plots of filtered and unfiltered total DDx TZW concentrations from Peeper samples are provided on Figure 5.5-1a. All sample results for summed and individual DDx isomers in TZW are presented in the SCRA database (Appendix A3) and are summarized in Appendix D4, Table D4-1.

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~~Total DDx concentrations in the six shallow peeper and six filtered Trident samples ranged from below detection limits (detection limits ranged from 0.0042 UA µg/L to 0.035 UA µg/L) to 0.158 J µg/L. The highest filtered shallow DDx concentration was measured at RP-03-C, at the downstream Rhone Poulenc site. Only one filtered, deep Trident sample was collected (at RP-03-C); this sample had a total DDx concentration of 0.179 J µg/L.~~

~~Total DDx concentrations in the eight shallow unfiltered Trident samples ranged from 0.0075 JA µg/L to 3.05 J µg/L. The highest (>3 µg/L, shown as red symbols on Map 5.4-1) unfiltered shallow DDx concentration was measured at AP-03-A (3.05 J µg/L).~~

²⁰ Note that 2,4'-DDD, 2,4'-DDE, and 2,4'-DDT were not sampled during the 2004 Pilot Study; therefore, the total DDx sum for these samples consists of only the 4,4'-DDx isomers. These results are distinguished with an "A" qualifier on Map 5.4-1.

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The three unfiltered deep-DDx sample concentrations ranged from 0.169 J µg/L to 5.73 J µg/L, with the highest deep concentration collocated with the highest shallow concentration at AP-03-A. Patterns and trends in the data set are discussed in the following subsection.

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5.5.59.0 Patterns and Trends of DDx in TZW

Patterns and trends of DDx distribution are evaluated based on maps and stacked bar charts, as described in Section 5.4.3. Evaluation of these patterns and trends for DDx is limited due to low sample size and detection frequencies; however, development of basic conclusions regarding chemical composition and the influence of filtration and sample depth is possible, as presented in the following paragraphs.

As shown on the histograms on Map 5.4-1 and described above, the observed ranges of DDx concentrations are generally higher in unfiltered samples as compared to the observed range for filtered and peeper samples. This tendency observed in the histogram ranges is upheld in a point-by-point assessment of the seven collocated filtered and unfiltered Trident pairs, where unfiltered sample concentrations are over 90 percent greater than filtered samples in four pairs collected offshore of the Arkema Acid Plant area. Higher sample concentrations in unfiltered samples as compared to filtered samples is expected for these highly hydrophobic chemicals, indicating the presence of DDx sorbed to solids larger than the filter diameter (>0.45 µm) in the unfiltered Trident samples. These results indicate that the unfiltered samples in the former Acid Plant area are likely affected by intake of sediment in the unfiltered sampling process. Further, the highest filtered sample result is observed offshore of the Rhone Poulenc site, whereas the collocated unfiltered result offshore of the Rhone Poulenc site (0.21 J µg/L) is well below the average (1.78 µg/L) of all measured unfiltered concentrations; this result suggests that uptake of solids did not influence the unfiltered concentrations measured at RP-03-C.

Comparison of total DDx concentrations in unfiltered samples at the three sample locations (RP-03-C, AP-03-A, R2-AP-02) where both shallow (0 to 38 cm bml) and deep (90 to 150 cm bml) TZW samples were collected shows that the deeper samples consistently have higher concentrations than the shallow samples at AP-03-A and R2-AP-02. However, at RP-03-C the deeper sample is generally comparable to the corresponding shallow samples in both filtered and unfiltered data sets.

Figure 5.4-1 presents bar charts showing percent composition of the six DDx congeners in the 15 samples with a detected total DDx result. The chart only presents samples where all six DDx congeners were analyzed.²⁴ Samples are organized along the x-axis in groups referring to groundwater discharge zones. (These zones are indicative of areas of similar groundwater discharge conditions, as described in Appendix C2.) On these figures, sample IDs indicate sample location, sample method, sample depth, and

²⁴ The 2004 Pilot Study samples were analyzed for 4,4'-DDx congeners only, and are therefore not shown on the stacked bar chart in Figure 5.4-1.

field duplicates, as described above in Section 5.4.3. Evaluation of the stacked bar chart in Figure 5.4.1 yields the following observations:

- The two duplicate sample pairs (AP-03-A-TR-f and AP-03-A-TR-f-dup; AP-03-A-TR-uf and AP-03-A-TR-uf-dup) show good reproducibility in composition trending.
- Two of the three shallow and deep sample pairs show similar compositions at both depths. The shallow and deep pair collected at R2-AP-02-TR-uf has an extreme concentration difference and shows different composition between the shallow and deep result.
- The bar chart trends further support the overall observed trends noted above in discussions of spatial distribution and filtration effects. The highest total DDx concentrations (concentration indicated by the black line corresponding to the right y-axis) are mainly associated with unfiltered samples (filtered sample IDs are highlighted). These total concentration peaks (designated by the black line) correspond to DDx compositions dominated by 4,4'-DDT plus 4,4'-DDD.

In summary, for the limited data set available, the highest DDx concentrations were observed in unfiltered deep (90 to 150 cm bml) samples collected offshore of the former Acid Plant area. Filtration greatly reduced DDx concentrations measured offshore of the Acid Plant, indicating that DDx is present on solids. The highest filtered sample result is observed offshore of the Rhone-Poulenc site. Filtration did not significantly reduce DDx concentrations measured at the single Rhone-Poulenc sample location, and the unfiltered results offshore of the Rhone-Poulenc site are below the average of unfiltered concentrations observed offshore of the former Acid Plant site. Further, offshore of the former Acid Plant area, TZW concentrations are generally greater at depth (90 to 150 cm bml) as compared those in shallow TZW (0 to 38 cm bml). Conclusions about completeness of the groundwater pathway are presented in detail with additional lines of evidence in Appendix C2 and summarized in Section 4.

5.5.67 5.5.1.6 Total PAHs in TZW

The following subsections present the in-river distribution of PAHs in TZW samples and note patterns and trends in this data set. The TZW IC list includes total PAHs, HPAHs, cPAHs, BaPEq, as well as individual PAHs BAP and naphthalene. LPAHs are also discussed here to provide for complete discussion of total PAHs and HPAHs, though they are not on the IC list for TZW. The physical properties and behavior patterns of individual PAHs vary with molecular weight, with the larger PAHs exhibiting more hydrophobicity and a stronger tendency to adsorb to sediments.

5.5.67.1 Observed Chemical Distribution of PAHs in TZW

In the Round 2 GWPA SAP (Integral et al. 2005), PAHs were identified as an upland groundwater COI for sampled at six of the nine TZW study sites: Kinder Morgan,

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ARCO, ExxonMobil, Gasco, Siltronic, and Willbridge Terminal. The discussion below focuses on Total PAH results, which are summarized in Table 5.5-1. TZW samples for individual PAHs, total PAHs, HPAHs, and cPAHs were collected at a total of 53 individual sample locations offshore of these sites during the 2004 Pilot Study and 2005 GWPA sampling events. Twenty-two locations were sampled for individual PAHs and PAH sums by Gasco in 2007 (Anchor 2008b), and 13 locations were sampled by Siltronic in 2005 (HAI 2005a; MFA 2005a). An additional 24 deep (90 cm bml) naphthalene samples were also collected by Siltronic. All sample results for summed and individual PAH parameters in TZW are presented in the SCRA database (Appendix A3) and are summarized in Appendix D4, Table D4-1. HPAHs, LPAHs, cPAHs, BaPEq, as well as individual PAH results, are presented in Appendix D4, Table D4-1. The discussion below focuses on Total PAH results, which are summarized in Table 5.5-1.

Total PAH data collected within the Study Area offshore of the six sites referenced above include results from the following samples:

- 24 Peeper samples (0 to 38 cm bml), including 6 duplicates;
- 81 shallow (0 to 30 cm bml) Trident samples, including 15 duplicates, collected from 35 locations (with collocated filtered and unfiltered samples collected at 31 locations);
- X deep (60 to 150 cm bml) Trident samples in this data set (with collocated filtered and unfiltered samples collected at X locations); and
- X unfiltered samples collected with a Geoprobe from depths of 0 to 90 cm bml.

PAHs were detected in TZW samples offshore of all six sites. Total PAHs were identified in all of the Peeper samples, with concentrations ranging from 0.105 J ug/L at KM10APR to 300 J ug/L at GS01BPR, which are offshore of Kinder Morgan and Gasco, respectively. Total PAHs were identified in all but 3 of the shallow Trident unfiltered samples with concentrations ranging from 0.0025 J ug/L at EM02ATR to 1,200 J ug/L at GS02ATR, which are offshore of ARCO and Gasco, respectively. Total PAHs were identified in all but two of the shallow Trident filtered samples with detected concentrations ranging from 0.0031 J ug/L at W09ATR to 3,490 NJ ug/L at GS07BTR, which are offshore of Willbridge Terminal and Siltronic, respectively.

These The Total PAH sample results are presented on Maps 5.45-2a-e, 5.4-3a-d, 5.4-4a-d, and 5.4-5a-e, for PAHs (including LPAHs and HPAHs), cPAHs (including BaPEq values), BAP, and naphthalene, respectively. Each The map set presents filtered (top panel) and unfiltered (bottom panel) TZW results, where available, with inset histograms summarizing the distribution of samples shown on each map relative to the distribution across the TZW data set. There are 34 collocated filtered and unfiltered Trident sample pairs, and there are seven deep (90 to 150 cm bml) Trident samples in

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this data set. For naphthalene, there are an additional 24 deep (90 cm bml) samples collected from RM 6 to 7. For total PAHs, ePAHs, and BAP, sample results collected between RM 6 and 7 are presented on two maps to allow for presentation of all sample concentration results in this densely sampled area (the first map shows concentration labels for LWG-collected data, and the second map shows concentration labels for non-LWG collected data). Observed PAH concentration ranges varied among the offshore study areas, with the highest total PAH concentrations consistently being observed offshore of the Gasco and Siltronic sites. The lowest range of TZW PAH concentrations was observed offshore of the Willbridge Terminal site. These relative concentration ranges are apparent on the inset histograms on Maps 5.5-2a-e.

Scatter plots of filtered and unfiltered total PAH TZW concentrations from Peeper samples are provided on Figure 5.5-1b. These figures show sample concentrations along an x-axis noting the river mile of each sample location. Color-coded symbols distinguish sample type and depth. Paired plot sets are presented for each chemical to show filtered and unfiltered results, where available.

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Naphthalene sample results are presented on Maps 5.4-5a-e. Naphthalene is a two-ring LPAH, and has the lowest molecular weight of all the PAHs. Naphthalene data were collected as part of VOC sample analysis (EPA method SW8260), as well as PAH sample analysis (EPA method 8270), and therefore naphthalene was sampled at more locations (160) than other individual PAHs or total PAH sums (88 locations). Where naphthalene results were generated using both analysis techniques, the method 8260 results are presented.²² Due to its high volatility, only unfiltered sample results are presented on Maps 5.4-5a-e. For naphthalene, sample results collected between RM 6 and 7 are presented on three maps (Map 5.4-5b presents all shallow sample results; Map 5.4-5c is a zoom-in to show shallow sample results in the most densely sampled area; Map 5.4-5d presents all deep sample results).

5.5.67.1.1 — Total PAHs

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PAHs were detected in TZW samples offshore of all six sites. Total PAH values observed in TZW cover a large concentration range. In shallow filtered Trident and peeper samples, concentrations ranged from detection limits (0.042 U µg/L to 0.073 U µg/L) to 1,200 J µg/L; in unfiltered Trident and Geoprobe samples, concentrations ranged from detection limits (0.036 U µg/L to 0.043 U µg/L) to 15,100 JA µg/L. The highest PAH sample results were observed offshore of the Gasco and Siltronic sites, with the maximum filtered result measured at GS-02-A, at the downstream end of the Gasco site. The highest (>1,000 µg/L; shown as red symbols on Maps 5.4-2a-e) unfiltered concentrations of total PAHs in TZW were observed at stations GP-73 (15,100 JA µg/L), GP-68 (13,100 JA µg/L), GP-64 (12,600 JA µg/L);

²² Seventy-eight naphthalene samples were analyzed with both 8260 and 8270 methods. Of these, 49 samples were below detection limits for both methods. For the 19 samples which were detected with both methods, higher concentrations were found with method 8260 in 73% of the samples.

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and GP-69 (12,100 JA $\mu\text{g/L}$), all located roughly offshore of the property line between the Gasco and Siltronic sites. Unfiltered, deep Trident (90 to 150 cm bml) total PAH sample concentrations ranged from 0.67 to 430 $\mu\text{g/L}$, with the highest deep concentration at GS-08-D, also located offshore of the property line between the Gasco and Siltronic sites. No filtered deep Trident samples were collected.

Observed PAH concentration ranges varied substantially among the offshore study areas, with the highest total PAH concentrations consistently being observed offshore of the Gasco (up to 15,100 JA $\mu\text{g/L}$) and Siltronic (up to 13,100 JA $\mu\text{g/L}$) sites. The lowest range of TZW PAH concentrations was observed offshore of the Willbridge Terminal site. These relative concentration ranges are apparent on the inset histograms on Maps 5.4-2a-e.

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5.5.67.1.2 — LPAHs and HPAHs

LPAH and HPAH components of the total PAH sum are shown in concentration labels on Maps 5.4-2a-e. These maps indicate that LPAH concentrations are consistently higher than HPAHs in TZW sampled across the Study Area. Further, LPAH concentrations show similar spatial patterns to the total PAH concentrations.

In peeper and filtered Trident samples, HPAH concentrations range from detection limits (0.0071 U $\mu\text{g/L}$ to 0.38 U $\mu\text{g/L}$) to 7.6 J $\mu\text{g/L}$, while LPAH concentrations range from detection limits (0.042 U $\mu\text{g/L}$ to 0.073 U $\mu\text{g/L}$) to 1,190 $\mu\text{g/L}$. In unfiltered Trident and Geoprobe samples, HPAH concentrations covered a higher range, from detection limits (0.036 U $\mu\text{g/L}$ to 0.66 U $\mu\text{g/L}$) to 880 $\mu\text{g/L}$, as did LPAH concentrations, ranging from detection limits (0.016 U $\mu\text{g/L}$ to 0.069 U $\mu\text{g/L}$) to 14,600 JA $\mu\text{g/L}$.

For both HPAH and LPAH sums, the highest results were recorded offshore of the Gasco and Siltronic sites. The highest unfiltered HPAH concentration was recorded at GS-B2 near the north end of the Gasco site. The highest filtered and peeper HPAH concentrations were also measured in this area at GS-01-B (7.6 J $\mu\text{g/L}$) and GS-02-A (5.46 J $\mu\text{g/L}$). The highest unfiltered LPAH concentration was recorded at GP-73, roughly offshore of the property line between the Gasco and Siltronic sites. The highest filtered LPAH results were located at the north end of the Gasco site at GS-02-A (1,190 $\mu\text{g/L}$) and GS-01-B (290 $\mu\text{g/L}$).

5.5.67.1.3 — Total Carcinogenic PAHs

cPAH represents the sum of a subset of HPAHs and, as expected, the cPAH distribution follows that of HPAHs as shown on Maps 5.4-3a-d. In peeper and filtered Trident samples, cPAH concentrations range from detection limits (0.0024 U $\mu\text{g/L}$ to 0.017 U $\mu\text{g/L}$) to 0.64 J $\mu\text{g/L}$. In unfiltered Trident and Geoprobe samples, cPAH concentrations range from detection limits (0.0077 U $\mu\text{g/L}$ to 0.086 U $\mu\text{g/L}$) to 300 $\mu\text{g/L}$. The maximum filtered, peeper, and unfiltered cPAH concentrations measured were collocated with the maximum HPAH results at GS-02-A, GS-01-B, and GS-B2, respectively. Toxicity-weighted BaPEq concentrations range from detection limits (0.0018 U $\mu\text{g/L}$ to 0.028 U $\mu\text{g/L}$) to 70.3 $\mu\text{g/L}$. cPAH BaPEq concentrations are positively correlated with cPAH concentrations and maximum results were collocated with HPAH and cPAH maximum results.

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5.5.67.1.4 — Benzo(a)pyrene

BAP is a five-ring HPAH. Maps 5.4 4a-d show that the BAP spatial distribution follows that of HPAHs. In peeper and filtered Trident samples, BAP concentrations range from below detection limits (0.0018 U µg/L to 0.012 U µg/L) to 0.082 µg/L. In unfiltered Trident and Geoprobe samples, BAP concentrations range from detection limits (0.0021 U µg/L to 0.062 U µg/L) to 50 µg/L. The maximum filtered, peeper, and unfiltered BAP concentrations measured were collocated with the maximum HPAH results at GS-02-A, GS-01-B, and GS-B2, respectively.

5.5.67.1.5 — Naphthalene

Naphthalene is a two-ring LPAH, and has the lowest molecular weight of all the PAHs. Maps 5.4 5a-e present naphthalene concentrations for peeper, unfiltered Trident, and unfiltered Geoprobe samples. In unfiltered shallow Trident and Geoprobe samples, naphthalene concentrations range from detection limits (0.0063 U µg/L to 15 U µg/L²³) to 13,700 µg/L. The highest (>10,000 µg/L; shown as red symbols on Maps 5.4 5a-e) concentrations were observed offshore of the Gasco and Siltronic sites, with maximum shallow naphthalene concentrations collocated with or proximal to the maximum total PAH and LPAH locations at GP-73 (13,700 µg/L), GP-71 (12,400 µg/L), GP-68 (12,300 µg/L), and GP-64 (12,200 µg/L). Deep Trident (90 to 150 cm bml) and Geoprobe (91 cm bml) naphthalene sample concentrations ranged from detection limits (0.041 U µg/L to 150 U µg/L²⁴) to 11,200 µg/L, with the highest deep concentration at GP-76, also located offshore of the property line between the Gasco and Siltronic sites.

Patterns and trends in the data sets for total PAHs, cPAHs, BAP, and naphthalene are discussed in the following subsection.

Patterns and Trends of PAHs in TZW

As shown on the river mile specific portions of the histograms of Maps 5.4 2a-e and described above, the observed ranges of unfiltered total PAH concentrations for each river mile sampled are higher than filtered and peeper sampled concentrations. This trend is upheld in a point-by-point assessment of the 34 collocated filtered and unfiltered Trident pairs for total PAHs. Looking at the filtered and unfiltered Trident pairs, filtration decreased the average total PAH concentration by 24 percent, with a maximum decrease of up to 99 percent (AR-02-B). Note that the apparent large decrease in the total PAH concentration range with filtration seen on the harbor wide portion of the histograms is largely attributable to the lack of filtered PAH samples from the non-LWG investigations offshore of the Siltronic and Gasco sites. The Siltronic and Gasco unfiltered results account for most of the >1,000 µg/L values.

By examining the effects of filtration, the effects of individual PAH hydrophobicity can be seen in the data set. As shown on inset histograms on Maps 5.4 3a-d and 5.4 4a-d, the large,

²³ High detection limits were reported for six samples, all located offshore of the former Arkema-Acid Plant site and the Rhone-Poulenc site. The median detection limit for naphthalene for the entire TZW data set is 0.29 µg/L.

²⁴ See previous note above.

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hydrophobic cPAHs and BAP show extreme differences between filtered and unfiltered results (with an average of over 95 percent decrease in a paired sample comparison for both cPAHs and BAP), suggesting that these chemicals are present on solids $>0.45\ \mu\text{m}$ in diameter in unfiltered TZW samples. In contrast, the smaller, less hydrophobic individual PAHs have a lesser tendency to bind to sediment and would be expected to be less affected by filtration, contributing the lower net effect of filtration on total PAH concentrations. This filtration effect on total PAHs is therefore a function of the composition of each sample.

Comparison of total PAH concentrations in the seven collocated deep and shallow (0 to 38 cm bml) TZW samples shows that the unfiltered deep samples consistently exhibit higher concentrations than the corresponding shallow samples. In some cases, the unfiltered, deep sample concentrations are up to 2 orders of magnitude greater than the collocated shallow samples. The three filtered deep/shallow sample pair results, however, show no clear relative trend. As with total PAHs, analysis of collocated deep/shallow sample pair results shows that unfiltered concentrations of HPAHs, cPAHs, and BAP are generally much higher in deep samples. For naphthalene, 17 collocated deep (90 to 150 cm bml) and shallow (0 to 38 cm bml) Trident samples and 24 collocated deep (91 cm bml) and shallow (31 cm bml) Geoprobe samples were collected. In general, for the high ($>1,000\ \mu\text{g/L}$) concentration samples collected from RM 6 to 7, shallow samples showed somewhat higher concentrations than collocated deep samples. For other parts of the Study Area, no clear trends with depth were observed for naphthalene.

Stacked bar charts showing percent composition of detected total PAH sums are shown on Figures 5.4 2a-f. The charts present total PAH concentration (indicated by the black line corresponding to the right y axis), as well as the fraction of the total contributed by each of the 17 PAHs. Charts are presented for each relevant TZW study site, with samples organized along the x axis in groups referring to groundwater discharge zones. These zones are indicative of areas of similarly mapped groundwater discharge conditions offshore of the given study site and are presented and discussed in detail in Appendix C2.

There are a several patterns apparent in these stacked bar charts. First, duplicate sample pairs show good reproducibility in composition trending. Second, the shallow and deep pairs frequently show variable compositions, particularly in cases where the deeper concentration is greater than the shallow concentration (e.g., EM04C-TR-uf-150, which has an extreme concentration difference between the shallow and deep result). This may reflect weathering in the biologically active zone and/or differences in PAH composition in sediment with depth. Next, a distinct chemical composition is generally present at sample locations with very high total PAH concentrations. Acenaphthene is the dominant component of total PAH sums in most samples; however, at sample locations with total PAHs greater than $1,000\ \mu\text{g/L}$, naphthalene concentrations clearly dominate the composition. This result is interesting to evaluation of TZW because naphthalene is the most mobile chemical of the PAHs. This composition pattern is apparent in the bar charts for TZW data offshore of the Gasco and Siltronic sites (Figures 5.4 2d and 5.4 2e). These areas correspond to suspected discharge zones offshore of the Siltronic and Gasco sites (discussed in detail in Appendix C2).

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Composition trends with concentration and location are less apparent at the other TZW study sites, where total PAH concentrations cover a much lower concentration range.

In summary, of the sites sampled, total PAH concentrations were found to be highest offshore of the Gasco and Siltronic sites. Total HPAH, total ePAH, and BAP results showed similar distribution and filtration patterns. Because LPAHs tend to compose the majority of the total PAH concentrations, LPAH and naphthalene results generally followed the distribution patterns apparent for total PAHs. Filtration was observed to decrease the total PAH concentration slightly, with greater effects on the more hydrophobic PAHs, as expected. For total PAHs, total HPAH, total ePAH, and BAP, the unfiltered deeper (90 to 150 cm bml) Trident samples consistently showed higher concentrations than corresponding unfiltered shallow (0 to 38 cm bml) samples. Review of the fractional composition of the 17 individual chemicals that comprise total PAH shows a clear pattern of high naphthalene concentrations associated with high total PAH concentrations offshore of the Gasco and Siltronic sites. For these high-concentration naphthalene locations, shallow (31 cm bml) Geoprobe samples generally had slightly higher concentrations than the collocated deeper (91 cm bml) samples. Additional evaluation of PAHs in TZW is provided in the detailed, site-specific discussions of groundwater pathways in Appendix C2.

5.5.68 5.5.1.7 TPH in TZW/BEHP

TZW samples collected from the offshore areas of the nine study sites were not analyzed for BEHP.

5.5.1.8 Total Chlordanes

TZW samples collected from the offshore areas of the nine study were not analyzed for total chlordanes.

5.5.1.9 Aldrin

TZW samples collected from the offshore areas of the nine study sites were not analyzed for aldrin.

5.5.1.10 Dieldrin

TZW samples collected from the offshore areas of the nine study sites were not analyzed for dieldrin.

5.5.1.11 Arsenic

As part of the 2004 Pilot Study, Round 2 GWPA, and non LWG Gasco and Siltronic sampling efforts, TZW samples were analyzed for arsenic offshore of the at all nine TZW study sites. Sampling results for arsenic are presented on scatter plots in Figure 5.5-1c. These figures shows sample concentrations along an x-axis noting the river mile of each sample location. Color-coded symbols distinguish sample type and depth. Paired plot sets are presented for each chemical to show filtered and unfiltered results.

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where available. Additionally, arsenic results are presented on Maps 5.5-3a–e. The map set presents filtered (top panel) and unfiltered (bottom panel) TZW results, where available, with inset histograms summarizing the distribution of samples shown on each map relative to the distribution across the TZW data set.

As shown in Table 5.5-1, arsenic data collected ~~within the Study Area offshore of the nine sites referenced above~~ for TZW include results from the following samples:

- 39 Peeper samples (0 to 38 cm bml), including 10 duplicates;
- 60 shallow (0 to 30 cm bml) filtered Trident samples, including 11 duplicates;
- 64 shallow (0 to 30 cm bml) unfiltered Trident samples, including 11 duplicates;
- X deep (60 to 150 cm bml) Trident samples in this data set (with collocated filtered and unfiltered samples collected at X locations); and
- X unfiltered samples collected with a Geoprobe from depths of 0 to 90 cm bml.

Arsenic was detected in TZW samples offshore of all nine sites. Arsenic was detected in all but two of the Peeper samples, with concentrations ranging from 0.3 J ug/L (locations ARC03B, ARC06B-1, and ARC06B-2) to 17.2 ug/L at W04CPR. The maximum detected concentration was identified offshore of the Willbridge Terminal site. Arsenic was detected in 55 of the shallow Trident filtered samples, with detected concentrations ranging from 0.55 ug/L at W09ATR to 76.8 ug/L at EM03ATR, which are offshore of Willbridge Terminal and ExxonMobil, respectively. Arsenic was detected in all but 3 of the shallow Trident unfiltered samples with concentrations ranging from 0.72 ug/L at CP08BTR to 51.2 ug/L at W12ATR, which are offshore of Arkema and Willbridge Terminal, respectively.

5.5.1.12 Chromium

~~Samples collected during the 2004 Pilot Study, Round 2 GWPA at all nine TZW study sites, and non-LWG Gasco and Siltronic field events from locations offshore of the nine TZW study sites~~ were analyzed for chromium. Analytical results for chromium are presented on scatter plots in Figure 5.5-1d. These figures show sample concentrations along an x-axis noting the river mile of each sample location. Color-coded symbols distinguish sample type and depth. Paired plot sets are presented for each chemical to show filtered and unfiltered results, where available. Additionally, chromium results are presented on Maps 5.5-4a–e. The map set presents filtered (top panel) and unfiltered (bottom panel) TZW results, where available, with inset histograms summarizing the distribution of samples shown on each map relative to the distribution across the TZW data set.

As shown in Table 5.5-1, chromium data collected within the Study Area offshore of the nine sites referenced above include results from the following samples:

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- 39 Peeper samples (0 to 38 cm bml), including 10 duplicates;
- 62 shallow (0 to 30 cm bml) filtered Trident samples, including 11 duplicates;
- 65 shallow (0 to 30 cm bml) unfiltered Trident samples, including 11 duplicates;
- X deep (60 to 150 cm bml) Trident samples in this data set (with collocated filtered and unfiltered samples collected at X locations);
- X filtered samples collected with a Geoprobe from depths of 0 to 90 cm bml;
and
- X unfiltered samples collected with a Geoprobe from depths of 0 to 90 cm bml.

Chromium was detected in TZW samples collected from locations offshore of all nine sites. Chromium was detected in 17 of the Peeper samples, with concentrations ranging from 0.92 ug/L at location CP09DPR to 31.6 ug/L at CP07B, both of which were identified offshore of the Arkema site. Chromium was detected in 34 of the shallow Trident filtered samples, with detected concentrations ranging from 0.2 J ug/L at W09ATR to 98.3 ug/L at CP07B, which are offshore of Willbridge Terminal and Arkema, respectively. Chromium was detected in 45 of the shallow Trident unfiltered samples with concentrations ranging from 0.79 ug/L at SL03ATR to 122 ug/L at CP07B, which are offshore of Gasco and Arkema, respectively.

5.5.1.12 Copper

~~Samples collected during the 2004 Pilot Study, Round 2 GWPA, at all nine TZW study sites and non-LWG Gasco and Siltronic field events from locations offshore of the nine TZW study sites~~ were analyzed for copper. Analytical results for copper are presented on scatter plots in Figures 5.5-1e. These figures show sample concentrations along an x-axis noting the river mile of each sample location. Color-coded symbols distinguish sample type and depth. Paired plot sets are presented for each chemical to show filtered and unfiltered results, where available. Additionally, copper results are presented on Maps 5.5-5a-e. The map set presents filtered (top panel) and unfiltered (bottom panel) TZW results, where available, with inset histograms summarizing the distribution of samples shown on each map relative to the distribution across the TZW data set.

As shown in Table 5.5-1, copper data collected within the Study Area offshore of the nine sites referenced above include results from the following samples:

- 39 Peeper samples (0 to 38 cm bml), including 10 duplicates;
- 50 shallow (0 to 30 cm bml) filtered Trident samples, including 9 duplicates;
- 53 shallow (0 to 30 cm bml) unfiltered Trident samples, including 9 duplicates;

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- X deep (60 to 150 cm bml) Trident samples in this data set (with collocated filtered and unfiltered samples collected at X locations);
- X filtered samples collected with a Geoprobe from depths of 0 to 90 cm bml; and
- X unfiltered samples collected with a Geoprobe from depths of 0 to 90 cm bml.

Copper was detected in TZW samples collected from locations offshore of all nine sites. Copper was detected in 5 Peeper samples, with concentrations ranging from 1.63 ug/L at location ARC02B to 22.1 ug/L at CP07DPR. The maximum detected concentration was identified offshore of the Arkema site. The remaining four detected copper concentrations were identified in samples collected from locations offshore of ARCO.

Copper was detected in 10 of the shallow Trident filtered samples, with detected concentrations ranging from 0.36 ug/L at R2KM01TR to 3.63 ug/L at R2RP03TR, which are offshore of Kinder Morgan and Rhone Poulenc, respectively. Of the remaining 8 samples in which copper was detected, 3 were collected offshore of ExxonMobil, 2 were collected from locations offshore of Rhone Poulenc, 2 were collected from locations offshore of Willbridge Terminal, and 1 was offshore of ARCO. Copper was detected in 35 of the shallow Trident unfiltered samples with concentrations ranging from 1.54 ug/L at ARC02B to 63.1 ug/L at EM02CTR, which are offshore of ARCO and ExxonMobil, respectively.

5.5.1.12 Zinc

Samples collected during the 2004 Pilot Study, Round 2 GWPA, from all nine TZW study sites and non-LWG Gasco and Siltronic field events from locations offshore of the nine TZW study sites were analyzed for zinc. Analytical results for zinc are presented on scatter plots in Figures 5.5-1f. These figures show sample concentrations along an x-axis noting the river mile of each sample location. Color-coded symbols distinguish sample type and depth. Paired plot sets are presented for each chemical to show filtered and unfiltered results, where available. Additionally, zinc results are presented on Maps 5.5-6a–e. The map set presents filtered (top panel) and unfiltered (bottom panel) TZW results, where available, with inset histograms summarizing the distribution of samples shown on each map relative to the distribution across the TZW data set.

As shown in Table 5.5-1, zinc data collected within the Study Area offshore of the nine sites referenced above include results from the following samples:

- 39 Peeper samples (0 to 38 cm bml), including 10 duplicates;
- 60 shallow (0 to 30 cm bml) filtered Trident samples, including 11 duplicates;
- 64 shallow (0 to 30 cm bml) unfiltered Trident samples, including 11 duplicates;

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- X deep (60 to 150 cm bml) Trident samples in this data set (with collocated filtered and unfiltered samples collected at X locations):
- X filtered samples collected with a Geoprobe from depths of 0 to 90 cm bml; and
- X unfiltered samples collected with a Geoprobe from depths of 0 to 90 cm bml.

Zinc was detected in TZW samples collected from locations offshore of all nine sites. Zinc was detected in 18 Peeper samples, with concentrations ranging from 7.11 J ug/L at location R2KM02PR, which is offshore of Kinder Morgan, to 418 ug/L at R2CP01PR. The maximum detected concentration was identified offshore of the Arkema site.

Zinc was detected in 32 of the shallow Trident filtered samples, with detected concentrations ranging from 0.95 ug/L at R2KM01TR to 526 ug/L at R2AR01TR, which are offshore of Kinder Morgan and ARCO, respectively. Zinc was detected in 39 of the shallow Trident unfiltered samples with concentrations ranging from 7.81 J ug/L at W09ATR to 556 ug/L at R2AR01TR, which are offshore of Willbridge Terminal and ARCO, respectively.

5.5.1.12 TBT

TZW samples collected from the offshore areas of the nine study sites were not analyzed for TBT. The following subsections present the in-river distribution of TPH results in TZW samples, as well as a discussion of patterns and trends in this data set. The TZW IC list includes DRH, RRH, and GRH. TPH is not a TZW IC, but it is presented and discussed here to support the discussion of the distribution and patterns of the components. TPH, as analyzed for the Round 2 investigation, is the measure of all hydrocarbons and non-hydrocarbons that can be quantified in the carbon range from n -C₆ to n -C₃₈. Likewise, the components (DRH, RRH, and GRH) are simply descriptive laboratory terms for the fractions of TPH, and not source assignments or indications of toxicity. Further, the TPH data contain hydrocarbons of both natural and anthropogenic origin.

5.5.68.1 Observed Chemical Distribution of TPH in TZW

In the Round 2 GWPA SAP (Integral et al. 2005), TPH was identified as an upland groundwater COI for six of the nine TZW study sites: Kinder Morgan, ARCO, ExxonMobil, Gasco, Siltronic, and Willbridge Terminal. Shallow TZW samples for TPH were collected at a total of 47 individual sample locations offshore of these sites during the 2004 Pilot Study and 2005 GWPA sampling events. Paired filtered and unfiltered samples were collected at 30 of these locations, and deep samples (90 to 150 cm bml) were collected at eight of these locations. TPH was not sampled during the non-LWG TZW investigations at Siltronic in 2005 (MFA 2005a,b) and Gasco in 2007 (Anchor 2008b).

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Sample results are presented on Maps 5.4-6a-d, including distinction in the flyout boxes of diesel range, residual range, and gasoline range fractions of TPH. These maps present filtered (top panel) and unfiltered (bottom panel) TZW results, where available, with inset histograms summarizing the distribution of samples shown on each map relative to the distribution across the entire Study Area. Note that gasoline range fractions of TPH are volatile, and were therefore not evaluated for filtered samples. All summed and individual TPH sample results for TZW are presented in the SCRA database (Appendix A3) and are summarized in Appendix D4, Table D4-1.

TPH was detected in TZW samples offshore of all six of the studied sites. TPH values observed in TZW cover a fairly large concentration range, varying from undetected (detection limits ranged from 0.058 U mg/L to 0.26 U mg/L) to 4.1 J mg/L in filtered Trident and peeper samples. In unfiltered Trident samples, observed concentrations ranged from undetected (detection limits ranged from 0.038 U mg/L to 0.18 U mg/L) to 11.3 J mg/L. The highest concentrations of TPH in TZW were observed offshore of the Gaseo and Siltronic sites, with the highest unfiltered Trident concentrations of TPH observed at Gaseo locations GS-07-B (11.3 J mg/L) and GS-02-A (6.01 J mg/L) in unfiltered samples, and the highest filtered or peeper TPH results observed at Gaseo location GS-02-A (4.1 J mg/L) and Siltronic location SL-04-F (2.35 J mg/L). The lowest range of TZW TPH concentrations were observed offshore of the Willbridge Terminal site.

5.5.68.2 Patterns and Trends of TPH in TZW

As shown on the histograms of the TPH map series, the distribution of unfiltered samples covers a larger and higher concentration range than the distribution of filtered samples; however, it should be noted that filtered TPH values do not include GRH (per sampling protocols for VOCs, filtered samples of GRH were not collected). Focusing on DRH and RRH (Table D4-1), it is clear, however, that filtration consistently decreases the concentration of these components. Further interpretation of this apparent effect of filtration is complicated by the expected variability in TPH composition (and corresponding hydrophobicity) from site to site (and likely sample to sample). As noted above, TPH, as analyzed for the Round 2 investigation, is simply the measure of all hydrocarbons and non-hydrocarbons that can be quantified in the carbon range from $n\text{-C}_6$ to $n\text{-C}_{28}$, with no distinction/identification of specific component chemicals.

Comparison of TPH concentrations in the eight deep sample locations (90 to 150 cm bml) with the corresponding shallow results (0 to 38 cm bml) shows deep unfiltered results to be generally greater than shallow unfiltered results. Filtered deep results, however, show no clear trend. As discussed in Appendix C2, this information was evaluated in greater detail for each TZW study site in the consideration of groundwater pathway along with other lines of evidence.

To support consideration of patterns in the fractional composition of TPH, stacked bar charts are presented in Figures 5.4-3a-f, with one figure for each relevant TZW study

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site. Each figure presents results grouped by interpreted groundwater discharge zones. These zones are indicative of areas of similarly mapped groundwater discharge conditions offshore of the given study site and are discussed in detail in Appendix C2. These figures present both filtered and unfiltered results, with filtered sample IDs highlighted. As noted above, the filtered results for TPH do not contain GRH fractions. A general review of these figures reveals that, with few exceptions, duplicate results (indicated by “dup” in the sample ID) show similar composition and total concentration to the original sample.

Looking at the bar chart results site by site, there are few notable patterns in these plots relative to the interpreted zoning of groundwater discharge. Offshore of the Siltronic site, the “offshore discharge zone,” where there is a complete pathway for groundwater discharge of select VOCs (discussed in Appendix C2), shows a fairly clear TPH composition shift toward GRHs, as compared to the samples from the other Siltronic zones. (Note again that the highlighted filtered samples do not contain GRH in the TPH composition presented.) Similar increases in GRH fractional composition of TPH can be seen in samples offshore of the Gaseo, ARCO, and ExxonMobil sites; however, dominance of the TPH concentration in these unfiltered samples offshore of these sites is also generally accompanied by a sharp decrease in TPH concentration, making the pattern more difficult to interpret (possibly more reflective of the lack of DRH and RRH than any increase in GRH). Further, these concentration ranges are close to detection limits, and the GRH results typically have lower detection limits (the average gasoline range detection limit was 0.06 mg/L compared to 0.14 and 0.16 mg/L for RRH and DRH samples).

In summary, the general nature of the analyte TPH (unknown mixture of anthropogenic and natural hydrocarbons and non-hydrocarbons that can be quantified in the carbon range from $n\text{-C}_6$ to $n\text{-C}_{38}$) significantly confounds detailed, source-related interpretation of results. Overall, filtration was observed to decrease the DRH and RRH fractions. Review of the fractional components (DRH, RRH, and GRH) showed a composition shift toward GRH in the offshore discharge zone at the Siltronic site; however, patterns elsewhere were generally weak and more difficult to interpret when TPH concentration changes were also considered. Site-specific conclusions about groundwater pathway are presented in detail with additional lines of evidence in Appendix C2 and summarized in Section 4.

5.5.69 Additional Indicator Chemicals in TZW

The following subsections present brief descriptions of the in-river distribution of TZW ICs not on the Study Area-wide bounding chemical list (total PCBs, total PCDD/Fs, total DDx, total PAHs). Note that the bounding ICs were not the focus chemicals at all TZW study sites and were not sampled at many of the sites. As described in the introduction to Section 5.4, the distribution of additional ICs in TZW is briefly discussed here. These additional ICs are grouped by chemical type, where possible, in the subsequent discussions. Supporting maps are presented for all chemicals. All

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sample results for TZW are presented in the SCRA database (Appendix A3) and are summarized in Appendix D4, Table D4-1.

5.5.69.1 — Silvex in TZW

Samples were analyzed for the herbicide Silvex in TZW in the vicinity of the former Rhone Poulenc plant. The sampling results for Silvex in TZW are shown on Map 5.4-7. Seven locations were sampled in the shallow TZW (0 to 38 cm bml), and 2 collocated deeper samples were collected (90 to 150 cm bml). Additionally, six collocated filtered samples were collected.

Silvex was detected in 27 percent of the samples. Silvex concentrations in TZW samples ranged from undetected (detection limits ranged from 0.06 U µg/L to 0.37 U µg/L) to 22 µg/L, with the maximum concentration measured at RP-03-E. All Silvex detections were located within a zone identified as an offshore groundwater discharge zone for the Rhone Poulenc site. This zone is presented in Section 4 and discussed in detail in Appendix C2, along with the lines of evidence used to make this determination.

5.5.69.2 — Cyanide in TZW

Samples were analyzed for cyanide in TZW offshore of only the Gasco and Siltronic sites during the Round 2 GWPA sampling effort and during the two non-LWG sampling efforts (Anchor 2008b; MFA 2005a,b). The sampling results for cyanide in TZW are shown on Map 5.4-8. Fifty-two locations were sampled offshore of these two sites for cyanide, and three paired deep (90 to 150 cm bml) samples were collected. For cyanide, only unfiltered samples were collected. Total cyanide, very soluble and chemically stable, is not expected to adsorb significantly to solids. Measurements of the most toxic form of cyanide, free cyanide, were made offshore of the Gasco and Siltronic sites as part of the non-LWG 2007 investigation (Anchor 2008b); however, free cyanide was only detected in one of those samples (GS-B2). Free cyanide is discussed in detail in the *Offshore Investigation Report, NW Natural "Gasco" Site* (Anchor 2008b).

Total cyanide was detected in 95 percent of the TZW samples. Cyanide concentrations ranged from undetected (detection limits ranged from 0.003 U mg/L to 1.4 U mg/L) to 23.1 U mg/L, with the maximum concentration observed at GS-02-A. Cyanide concentrations in the three deeper TZW samples (90 to 150 cm bml) were comparable to the concentrations observed in the shallow (0 to 38 cm bml) samples. Site specific conclusions about groundwater pathway are presented in detail with additional lines of evidence in Appendix C2.

5.5.69.2 — Perchlorate in TZW

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Samples were analyzed for perchlorate in TZW only offshore of the former Chlorate Plant and former Acid Plant areas of the Arkema site. The sampling results for perchlorate in TZW are shown on Map 5.4-9. Twenty locations were sampled in the shallow TZW (0 to 38 cm bml), and seven samples were collected in deeper TZW (90 to 150 cm bml). Only unfiltered samples were collected, since perchlorate is ionic and not expected to adsorb significantly to solids.

Perchlorate was detected in 52 percent of the samples. Perchlorate concentrations in shallow TZW samples ranged from undetected (detection limits ranged from 0.4 U µg/L to 20,000 U µg/L²⁵) to 177,000 µg/L; and the maximum deeper (90 to 150 cm bml) sample concentrations ranged from undetected (detection limits ranged from 40 U µg/L to 40,000 U µg/L²⁶) to 210,000 µg/L. These values are comparable to or higher than those observed in the upland nearshore groundwater. Perchlorate concentrations in the deeper TZW samples (90 to 150 cm bml) collected offshore of the Arkema site were often higher than in the collocated shallower samples (0 to 38 cm bml). The highest (>100,000 µg/L; shown as red symbols on Map 5.4-9) perchlorate concentrations were found along transect 7 (sampling locations CP-07-A, CP-07-B, and CP-07-D).

5.5.69.3 Metals in TZW

The TZW IC list includes eight metals: arsenic, barium, cadmium, copper, lead, manganese, nickel, and zinc. As part of the 2004 Pilot Study, Round 2 GWPA, and non-LWG Gasco and Siltronic sampling efforts, samples were analyzed for metals at all nine TZW study sites. Where sample volumes permitted in the Round 2 GWPA sampling effort, filtered samples were also collected; however, only three filtered metals samples were collected as part of the non-LWG investigation offshore of the Gasco and Siltronic sites. This distinction is important to note when reviewing the paired figures showing filtered and unfiltered results for each metal. In all, 126 locations were sampled for metals. Of these, filtered pairs were collected at 62 locations and paired deep samples (90 to 150 cm bml with Trident) were collected at 22 locations.

Sampling results for metals are also presented on scatter plots in Figures 5.4-4a-h. These figures show sample concentrations along an x-axis noting the river mile of each sample location. Color-coded symbols distinguish sample type and depth. Paired plot sets are presented for each chemical to show filtered and unfiltered results, where available. Additionally, arsenic, copper, and zinc results are presented on Maps 5.4-10a-e, 5.4-11a-e, and 5.4-12a-e, respectively, to support cross-media consideration in Section 10 (these are the TZW IC metals that are also included on the CSM IC list, Table 5.0-2).

²⁵ High detection limits (4,000 U µg/L, 20,000 U µg/L, and 40,000 U µg/L) were reported for 3 samples, all located offshore of the former Arkema Acid Plant site. The median detection limit for perchlorate for the entire TZW data set is 10 µg/L.

²⁶ See note 23 above.

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5.5.71.0.0 — Arsenic Distribution

Arsenic TZW results are shown on Figure 5.4 4a and Maps 5.4 10a-e. Arsenic was detected in 88 percent of TZW samples, and detection limits ranged from 0.2 U µg/L to 20 U µg/L. Detected arsenic concentrations ranged from 0.3 J µg/L to 77.3 µg/L, with an average concentration of 11.1 µg/L. Both filtered and unfiltered arsenic concentrations spanned generally consistent ranges across the Study Area. Evaluation of paired filtered and unfiltered detected samples shows that filtration decreases the total arsenic concentration by 16 percent on average. Deep (90 to 150 cm bml) Trident samples showed higher concentrations than collocated shallow (0 to 38 cm bml) samples in 17 of 24 collocated deep/shallow sample pairs. The tendency of arsenic compounds to associate with sediment particles can be highly variable and is strongly influenced by redox chemistry and microbial processes. A more detailed biogeochemical discussion of arsenic in TZW, sediments, and upland groundwater is presented in Appendix C2.

5.5.73.0.0 — Barium Distribution

Barium TZW results are shown on Figure 5.4 4b. Barium was detected in 99 percent of TZW samples. Detected barium concentrations ranged from 4.06 to 4,630 µg/L, with an average concentration of 334 µg/L. The highest (>1,000 µg/L) peeper, unfiltered Trident, and unfiltered push probe barium concentrations were observed offshore of the Gasco, Arkema, and Rhone Poulenc sites, while notably high filtered barium measurements were observed offshore of the Arkema site. Evaluation of paired filtered and unfiltered detected samples shows that filtration decreases the total barium concentration by 38 percent on average. Deep (90 to 150 cm bml) Trident samples showed higher concentrations than collocated shallow (0 to 38 cm bml) samples in 14 of 24 collocated deep/shallow sample pairs. The tendency of barium compounds to associate with sediment particles can be highly variable and is strongly influenced by redox chemistry and microbial processes. A more detailed biogeochemical discussion of barium in TZW, sediments, and upland groundwater is presented in Appendix C2.

5.5.75.0.0 — Cadmium Distribution

Cadmium TZW results are shown on Figure 5.4 4c. Cadmium was detected in 68 percent of TZW samples, with detection limits ranging from 0.002 U µg/L to 0.2 U µg/L and detected concentrations ranging from 0.004 J µg/L to 36 µg/L. The average cadmium concentration is 0.45 µg/L. The highest (>1.5 µg/L) peeper, unfiltered Trident, and unfiltered push probe cadmium concentrations were observed offshore of the Arkema (former Chlorate Plant area), Gasco, and Siltronic sites, while filtered Trident and push probe cadmium concentrations were consistently low across the Study Area. Evaluation of paired filtered and unfiltered detected samples shows that filtration decreases the total cadmium concentration by 53 percent on average. Deep (90 to 150 cm bml) Trident samples showed higher concentrations than collocated shallow (0 to 38 cm bml) samples in 9 of 24 collocated deep/shallow sample pairs. Neither the filtered nor unfiltered Trident samples exhibited consistent trends with depth.

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5.5.77.0.0 — Copper Distribution

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Copper TZW results are shown on Figure 5.4 4d and Maps 5.4 11a-e. Overall, copper was detected in 51 percent of TZW samples, and detection limits ranged from 0.08 U µg/L to 32.9 U µg/L. Detected peeper, Trident, and push probe copper concentrations ranged from 0.28 to 555 µg/L, with an average concentration of 27.9 µg/L. The highest (>100 µg/L) concentrations were measured offshore of the Gaseco and Siltronic sites in push probe samples. The low (30 percent) detection frequency for filtered copper samples is evident in the lower plot on Figure 5.4 4d, with few detected filtered copper samples observed across the Study Area. Evaluation of paired filtered and unfiltered detected samples shows that filtration decreases the total copper concentration by 92 percent on average, suggesting that most copper in the transition zone is associated with >0.45 µm particles. Deep (90 to 150 cm bml) Trident samples showed higher concentrations than collocated shallow (0 to 38 cm bml) samples in 5 of 24 collocated deep/shallow sample pairs. Neither the filtered nor unfiltered Trident samples exhibited consistent trends with depth.

5.5.79.0.0 — Lead Distribution

Lead TZW results are shown on Figure 5.4 4e. Lead was detected in 55 percent of TZW samples, with detection limits ranging from 0.01 U µg/L to 20 U µg/L. Detected lead concentrations ranged from 0.01 J µg/L to 382 J µg/L, with an average concentration of 17.4 µg/L. The highest (>50 µg/L) total lead concentrations (peeper, unfiltered Trident, and unfiltered push probe) were observed offshore of the Gaseco, Siltronic, Arkema, and ARCO sites, while filtered Trident and push probe lead concentrations were consistently low across the Study Area. Evaluation of paired filtered and unfiltered detected samples shows that filtration decreases the total lead concentration by 97 percent on average, suggesting that most lead in the transition zone is associated with solids. Deep (90 to 150 cm bml) Trident samples showed higher concentrations than collocated shallow (0 to 38 cm bml) samples in 11 of 24 collocated deep/shallow sample pairs. Neither the filtered nor unfiltered Trident samples exhibited consistent trends with depth.

5.5.81.0.0 — Manganese Distribution

Manganese TZW results are shown on Figure 5.4 4f. Manganese was detected in all of the TZW samples collected, with a concentration range from 23 J µg/L to 66,200 µg/L and an average concentration of 4,930 µg/L. Filtered, peeper, and unfiltered manganese concentrations spanned generally consistent ranges across the Study Area. Filtration reduced manganese sample concentrations somewhat, with an average reduction of 22 percent for detected unfiltered and filtered sample pairs. Deep (90 to 150 cm bml) Trident samples showed higher concentrations than collocated shallow (0 to 38 cm bml) samples in 11 of 24 collocated deep/shallow sample pairs. Neither the filtered nor unfiltered Trident samples exhibited consistent trends with depth. The tendency of manganese compounds to associate with sediment particles can be highly variable and is strongly influenced by redox chemistry and microbial processes. A more detailed

biogeochemical discussion of manganese in TZW, sediments, and upland groundwater is presented in Appendix C2.

5.5.83.0.0 — Nickel Distribution

Nickel TZW results are shown on Figure 5.4 4g. Nickel was detected in 87 percent of TZW samples, and detection limits ranged from 0.2 UJ $\mu\text{g/L}$ to 20 U $\mu\text{g/L}$. Detected nickel concentrations ranged from 0.2 J $\mu\text{g/L}$ to 367 $\mu\text{g/L}$, with an average concentration of 18.5 $\mu\text{g/L}$. The highest ($>100 \mu\text{g/L}$) total nickel concentrations (peeper, unfiltered Trident, and unfiltered push probe) were observed offshore of the Gasco, Siltronic, and Arkema sites, while filtered Trident and push probe nickel concentrations were consistently low across the Study Area. Evaluation of paired filtered and unfiltered detected samples shows that filtration decreases the total nickel concentration by 49 percent on average. Deep (90 to 150 cm bml) Trident samples showed higher concentrations than collocated shallow (0 to 38 cm bml) samples in 8 of 24 collocated deep/shallow sample pairs. Neither the filtered nor unfiltered Trident samples exhibited consistent trends with depth.

5.5.85.0.0 — Zinc Distribution

Zinc TZW results are shown on Figure 5.4 4h and Maps 5.4 12a-e. Zinc was detected in 66 percent of TZW samples, with detection limits ranging from 0.78 UJ $\mu\text{g/L}$ to 16.4 U $\mu\text{g/L}$. Detected zinc concentrations ranged from 0.95 to 3,590 $\mu\text{g/L}$, with an average concentration of 113 $\mu\text{g/L}$. The highest ($>1,000 \mu\text{g/L}$) total zinc concentrations were observed offshore of the Gasco and Siltronic sites in unfiltered push probe samples, while the highest ($>20 \mu\text{g/L}$) filtered Trident and push probe zinc concentrations were measured offshore of the ARCO and Gasco sites. Evaluation of paired filtered and unfiltered detected samples shows that filtration decreases the total zinc concentration by 81 percent on average, suggesting that most zinc in the transition zone is associated with $>0.45 \mu\text{m}$ particles. Deep (90 to 150 cm bml) Trident samples showed higher concentrations than collocated shallow (0 to 38 cm bml) samples in 9 of 24 collocated deep/shallow sample pairs.

5.5.87.0.0 — Metals Patterns and Trends

In general, cadmium, copper, lead, nickel, and zinc in TZW showed a relatively consistent baseline range of concentrations offshore of all the nine TZW study sites, with relatively elevated levels offshore of a few of the study sites as shown on Figures 5.4 4a-h and Maps 5.4 10a-e, 5.4 11a-e, and 5.4 12a-e. Filtration reduced TZW concentrations by more than 50 percent for cadmium, copper, lead, nickel, and zinc. Both filtered and unfiltered arsenic and manganese concentrations spanned generally consistent ranges across the Study Area. The spatial distribution of metals likely reflects some combination of upland groundwater transport, local sediment redox conditions, and sediment contamination, varying by site and metal.

Filtration significantly and consistently reduced TZW sample concentrations for cadmium, copper, lead, nickel, and zinc, suggesting that much of the observed total

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concentration for these metals was associated with solid particles. Differences with filtration were not as pronounced for arsenic, barium, and manganese. (Note in review of Figures 5.4-4a-h, paired filtered results are not available for most samples collected offshore of the Gasco and Siltronic sites as part of the non-LWG investigations.) Analysis of collocated shallow (0 to 38 cm bml) and deep (90 to 150 cm bml) TZW results did not show consistent trends with depth for any of the metals.

Site-specific conclusions about groundwater pathways are presented in detail with additional lines of evidence in Appendix C2 and summarized in Section 4. Additionally, a geochemical analysis of arsenic, barium, and manganese is presented in Appendix C2 to further investigate the origin of the observed TZW concentrations. The geochemical analysis includes a statistical evaluation of the spatial distribution of these metals in TZW across the nine TZW study sites and a comparison of TZW concentrations with available upland groundwater concentrations. Geochemical controls on arsenic, barium, and manganese in TZW were evaluated by exploring correlations between metal concentrations and measured variables (e.g., pH, oxidation-reduction potential, alkalinity, and TOC) that could be expected to exert an influence upon their geochemical behavior. Geochemical modeling was performed to identify stable mineral and aqueous phases as a function of pH and Eh, mineral saturation indices, and mineral phases controlling the aqueous solubility of arsenic, barium, and manganese.

5.5.91.0—Chlorinated VOCs and SVOCs in TZW

The TZW IC list includes nine chlorinated VOCs (MCB; chloroethane; 1,2-DCA; 1,1,2-TCA; vinyl chloride; cis-1,2-DCE; TCE; chloroform; and methylene chloride) and one chlorinated SVOC (1,2-DCB). These VOCs were sampled offshore of all nine study sites as part of the 2004 Pilot Study, Round 2 GWPA, and non-LWG Gasco and Siltronic sampling efforts. In all, 150 locations were sampled for VOCs. Of these, paired deep (90 to 150 cm bml) Trident samples were collected at 18 locations throughout the Study Area, and 24 paired deep (91 cm bml) Geoprobe samples were collected offshore of Gasco and Siltronic. No filtered VOC or 1,2-DCB samples were collected, per sampling protocols for volatile compounds. Sampling results for these chemicals are presented spatially on Maps 5.4-13 through 5.4-18. Results are presented graphically for only those river miles where the chemicals were detected (Table 5.4-1 summarizes the mapped areas for each chemical). All sample results for VOCs and SVOCs in TZW are also presented in the SCRA database (Appendix A) and are summarized in Appendix D4, Table D4-1. Detailed site-by-site assessments of VOC concentrations with depth, along with other lines of evidence, are provided in Appendix C2 to support the assessment of groundwater pathway.

5.5.93.0.0—MCB and 1,2-DCB

Maps 5.4-13a-e present observed MCB and 1,2-DCB concentrations in TZW offshore of the sites where these analytes were detected (Gasco, Siltronic, Rhone-Poulenc, and Arkema; RM 6-7 and 7-8). Detected MCB concentrations ranged from 0.15 J µg/L to

30,000²⁷ µg/L, with the highest MCB concentrations (>1,000 µg/L; indicated by red symbols in the upper panels on Maps 5.4-13a-e) observed offshore of the Arkema site. Detected 1,2-DCB concentrations ranged from 0.14 J µg/L to 640 µg/L. The highest 1,2-DCB concentrations (>250 µg/L; indicated by red symbols in the lower panels on Maps 5.4-13a-e) were observed near Rhone Poulenc. There were no clear trends in sample concentration with depth for these chemicals across these study sites. The presence of both MCB and DCB offshore may be indicative of the chemicals' release and/or the degree of degradation that has occurred from 1,2-DCB to MCB.

5.5.95.0.0 — 1,2-DCA and 1,1,2-TCA

Maps 5.4-14a-b present observed 1,2-DCA and 1,1,2-TCA concentrations in TZW offshore of the sites where these analytes were detected²⁸ (Arkema and Gunderson; RM 7-8 and 8-9). For 1,2-DCA, there were seven detected observations offshore of the Arkema site and four detected observations offshore of the Gunderson site. Detected 1,2-DCA concentrations ranged from 0.13 J µg/L to 770 µg/L. The highest 1,2-DCA concentrations (>100 µg/L; indicated by red symbols in the upper panels on Maps 5.4-14a-b) were observed offshore of the Arkema area. 1,1,2-TCA was detected in three samples measured offshore of the Arkema site and four samples offshore of the Gunderson site. Detected 1,1,2-TCA concentrations ranged from 0.36 J µg/L to 400 µg/L.²⁹ The highest 1,1,2-TCA concentrations (>100 µg/L; indicated by red symbols in the lower panels on Maps 5.4-14a-b) were also observed offshore of the Arkema area. Detected concentrations in deeper Trident (90 to 150 cm bml) and Geoprobe (91 cm bml) were higher than concentrations observed in shallow samples (0 to 38 cm bml). The presence of both 1,1,2-TCA and 1,2-DCA offshore may be indicative of the chemicals' release and/or the degree of degradation that has occurred from 1,1,2-TCA to 1,2-DCA.

5.5.97.0.0 — Chloroethane and Vinyl Chloride

Maps 5.4-15a-f present observed chloroethane and vinyl chloride concentrations in TZW offshore of the sites where these analytes were detected (Siltronic, Rhone Poulenc, Arkema, and Gunderson; RM 6-7, 7-8, and 8-9). The highest concentrations of chloroethane (>100 µg/L; indicated by red symbols in the upper panels on Maps 5.4-15a-f) were observed offshore of the Gunderson site, and chloroethane was only sporadically detected offshore of the other sites. Detected chloroethane concentrations ranged from 0.23 J µg/L to 160 µg/L. In general, chloroethane detections were located in the same areas as TCA and particularly DCA detections, likely related to this degradation chain. Vinyl chloride was more widely detected, with the highest

²⁷ The maximum value of 30,000 µg/L was measured in a deep (90 to 150 cm bml) sample. The maximum shallow (0 to 38 cm bml) concentration was 12,000 µg/L. Only shallow samples were used in the loading analysis presented in Section 6.

²⁸ There were two or fewer detections for 1,2-DCA at RM 4-5 and at RM 6-7 for 1,1,2-TCA; therefore, these areas are not presented on maps.

²⁹ The maximum value of 400 µg/L was measured in a deep (90 to 150 cm bml) sample. The maximum shallow (0 to 38 cm bml) concentration was 360 µg/L. Only shallow samples were used in the loading analysis presented in Section 6.

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concentrations ($>100 \mu\text{g/L}$; indicated by red symbols in the lower panels on Maps 5.4 15a–e) observed offshore of the Siltronic and Arkema sites. Detected vinyl chloride concentrations ranged from $0.05 \text{ J } \mu\text{g/L}$ to $1,640 \mu\text{g/L}$ (GP 65; Siltronic), with the exception of higher concentrations measured in shallow ($4,300 \mu\text{g/L}$) and deep ($28,900 \mu\text{g/L}$) samples collected offshore of Siltronic at station GP 67.³⁰ In general, vinyl chloride detections were located in the same areas as TCE and particularly DCE detections, likely related to known degradation patterns for chlorinated solvents. There were no clear trends in sample concentration with depth for these chemicals offshore of these study sites.

5.5.99.0.0 — Chloroform and Methylene Chloride

Maps 5.4 16a–d present chloroform and methylene chloride concentrations in TZW offshore of the sites where these analytes were detected (Gaseo, Siltronic, Rhone Poulenc, Arkema, and Gunderson; RM 6–7, 7–8, and 8–9). The highest concentrations of chloroform ($>1,000 \mu\text{g/L}$; indicated by red symbols in the upper panels on Maps 5.4 16a–d) were observed offshore of the Arkema site. Chloroform concentrations ranged from undetected (detection limits ranged from $0.056 \text{ U } \mu\text{g/L}$ to $130 \text{ U } \mu\text{g/L}$) to $820,000 \mu\text{g/L}$ ³¹ (AP 03–A). The highest concentrations of methylene chloride ($>100,000 \mu\text{g/L}$; indicated by red symbols in the lower panels on Maps 5.4 16a–d) were also observed offshore of the Arkema site, with only sporadic detections offshore of other sites. Detected methylene chloride concentrations ranged from $0.23 \text{ J } \mu\text{g/L}$ to $520,000 \mu\text{g/L}$ (AP 03–B). For both of these chemicals, the deeper Trident (90 to 150 cm bml) and Geoprobe (91 cm) samples generally exhibited higher concentrations than the corresponding shallow TZW samples.

5.5.101.0.0 — cis-1,2-DCE and TCE

Maps 5.4 17a–f present cis-1,2-DCE and TCE concentrations in TZW offshore of the sites where these analytes were detected³² (Siltronic, Rhone Poulenc, Arkema, and Gunderson; RM 6–7, 7–8, and 8–9). The highest concentrations of cis-1,2-DCE ($>1,000 \mu\text{g/L}$; indicated by red symbols in the upper panels on Maps 5.4 17a–f) were observed offshore of the Siltronic site and the former Acid Plant area of the Arkema site. Detected cis-1,2-DCE concentrations ranged from $0.12 \text{ J } \mu\text{g/L}$ to $19,200 \mu\text{g/L}$ ³³ (GP 65), with the exception of higher concentrations measured in shallow ($67,000 \mu\text{g/L}$) and deep ($574,000 \mu\text{g/L}$) samples collected offshore of the Siltronic site

³⁰ GP-67 is located in an area which is understood to be impacted by historical direct discharges of TCE from an outfall and may not be representative of upland groundwater, as discussed in Appendix C2 and Section 10.

³¹ The maximum value of $820,000 \mu\text{g/L}$ was measured in a deep (90 to 150 cm bml) sample. The maximum shallow (0 to 38 cm bml) concentration was $770,000 \mu\text{g/L}$, measured at AP 03–B. Only shallow samples were used in the loading analysis presented in Section 6.

³² Note three low-level detections of TCE ($0.15 \text{ J } \mu\text{g/L}$ to $0.46 \text{ J } \mu\text{g/L}$) offshore of the ARCO site, and one low-level detection of cis-1,2-DCE ($0.59 \mu\text{g/L}$) offshore of the ExxonMobil site are not shown on maps.

³³ The maximum value of $19,200 \mu\text{g/L}$ was measured in a deep (91 cm bml) sample. The maximum shallow (30 cm bml) concentration was $14,400 \mu\text{g/L}$, also measured at GP 65. Only shallow samples were used in the loading analysis presented in Section 6.

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at GP-67.³⁴ The highest concentrations of TCE ($>1,000 \mu\text{g/L}$; indicated by red symbols in the lower panels on Maps 5.4-17a-f) were also observed offshore of the Siltronic site and the former Acid Plant area of the Arkema site. Detected TCE concentrations ranged from $0.14 \mu\text{g/L}$ to $7,100 \mu\text{g/L}$ ³⁵ (AP-03-A), with the exception of higher concentrations measured in shallow ($88,500 \mu\text{g/L}$) and deep ($585,000 \mu\text{g/L}$) samples collected at GP-67.³⁶ For the higher concentration ($>1,000 \mu\text{g/L}$) cis-1,2-DCE samples, the deeper (91 cm bml) Geoprobe samples had higher concentrations than collocated shallow (31 cm bml) Geoprobe samples. For TCE, the deeper Trident (90 to 150 cm bml) and Geoprobe (91 cm bml) samples generally exhibited higher concentrations than the corresponding shallow (0 to 38 cm bml) TZW samples.

5.5.103.0 Non-chlorinated VOCs in TZW

The TZW IC list includes two non-chlorinated VOCs, 1,2,4-trimethylbenzene and carbon disulfide. Maps 5.4-18a-e present 1,2,4-trimethylbenzene and carbon disulfide concentrations in TZW offshore of sites where these VOCs were present at concentrations above detection limits³⁷ (Gaseo and Siltronic from RM-6-7 for 1,2,4-trimethylbenzene; Gaseo, Siltronic, and Arkema from RM-6-8 for carbon disulfide).

Carbon disulfide was sampled at 150 locations offshore of all nine study sites. Of these, paired deep (90 to 150 cm bml) Trident samples were collected at 18 locations throughout the Study Area, and 24 paired deep (91 cm bml) Geoprobe samples were collected offshore of Gaseo and Siltronic. Detected concentrations of carbon disulfide in shallow peeper, Trident, and non-LWG push probe samples ranged from $0.15 \mu\text{g/L}$ to $800 \mu\text{g/L}$, with the two highest concentrations ($>10 \mu\text{g/L}$; indicated by red and orange symbols in the upper panels on Maps 5.4-18a-e) observed offshore of the northern end of the Gaseo site at locations GS-01-B ($800 \mu\text{g/L}$) and GS-02-A ($53 \mu\text{g/L}$). Due to low detection frequencies (only 1 detection in collocated shallow pairs), trends between the shallow (0 to 38 cm bml) and deeper (90 to 150 cm bml) Trident samples were not evaluated for carbon disulfide.

1,2,4-Trimethylbenzene samples were collected only during the Siltronic-led sampling event (MFA 2005a; HAI 2005a). In all, 41 locations were sampled with Geoprobe for 1,2,4-trimethylbenzene offshore of the Siltronic and Gaseo sites, and 24 collocated deep (91 cm bml) Geoprobe samples were also collected. No filtered samples were collected, per sampling protocols for VOCs. 1,2,4-Trimethylbenzene detected concentrations ranged from $1.04 \mu\text{g/L}$ to $69.9 \mu\text{g/L}$, with the maximum concentrations

³⁴ GP-67 is located in an area which is understood to be impacted by historical direct discharges of TCE from an outfall and may not be representative of upland groundwater, as discussed in Appendix C2 and Section 10.

³⁵ The maximum value of $7,100 \mu\text{g/L}$ was measured in a deep (90 to 150 cm bml) sample. The maximum shallow (0 to 38 cm bml) concentration was $48.7 \mu\text{g/L}$, measured at GP-65. Only shallow samples were used in the loading analysis presented in Section 6.48.7

³⁶ See note above.

³⁷ Note one low-level detection of carbon disulfide ($0.23 \mu\text{g/L}$) offshore of the Kinder Morgan site is not shown on maps.

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($>40 \mu\text{g/L}$; indicated by red symbols in the lower panels on Maps 5.4-18a-e) measured offshore of the property line between the Gasco and Siltronic sites. There were no clear trends in sample concentration with depth for 1,2,4-trimethylbenzene.

5.5.107.0 BTEX in TZW

Maps 5.4-19a-h present BTEX concentrations measured in TZW offshore of all nine study sites. The upper panel of each map presents the total BTEX concentration, and the lower half presents the relative contribution of each BTEX constituent (benzene, toluene, ethylbenzene, and xylenes) in the form of a pie chart.³⁸ To accommodate the large numbers of measurements taken between RM-6 and 7, this set of results is presented on four maps (Maps 5.4-19e-f). In all, BTEX was sampled in TZW at 150 locations, with 18 deeper (90 to 150 cm bml) paired Trident samples collected across the Study Area and 24 deep (91 cm bml) Geoprobe samples collected offshore of the Siltronic and Gasco sites. No filtered samples for BTEX constituent chemicals were collected, per sampling protocols for VOCs.

Across the study sites, total BTEX was detected in 75 percent of samples, with detected sample concentrations covering a large range, from $0.11 \text{ J } \mu\text{g/L}$ to $4,700 \mu\text{g/L}$ (GP-68); detection limits for undetected samples ranged from $0.22 \text{ U } \mu\text{g/L}$ to $11 \text{ U } \mu\text{g/L}$. The highest BTEX concentrations ($>1,000 \mu\text{g/L}$; indicated by red symbols in the upper panels on Maps 5.4-19a-h) were observed offshore of the Gasco and Siltronic sites, with one high value also observed offshore of Arkema (AP-04-D; $1,600 \mu\text{g/L}$). In general, there were no consistent patterns with depth in the paired shallow and deep samples.

The pie charts presented in the lower panels on Maps 5.4-19a-h present the relative concentration of BTEX constituent chemicals for each detected sample. No consistent patterns of BTEX composition related to spatial distribution or magnitude of total BTEX concentration were apparent across all nine TZW study sites. More localized patterns may be evident in the data, such as a general tendency for toluene and xylenes to dominate BTEX composition offshore of sites where generally lower concentrations (detection limits to $1.79 \text{ J } \mu\text{g/L}$) of BTEX were observed in TZW (Kinder Morgan Linnton, ARCO, ExxonMobil, and Willbridge Terminal). These results are considered and discussed in detail on a site-by-site and sample-by-sample basis in Appendix C2 to support the assessment of groundwater pathway at each study site.

5.5.1405.5.2 Groundwater Seeps

This section summarizes the location, available chemical data, and data quality assessment for upland groundwater seeps.

Groundwater seeps were assessed for the BHHRA because of the potential for humans to come into contact with seep water. The potential effects of human exposure to

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³⁸ The pie charts show only those constituent chemical concentrations that are above detection limits. If all components of the total BTEX sum are non-detect for a given sample, no pie chart is shown for that sample.

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~~groundwater discharge in surface seeps are presented in the initial BHHRA summary in Section 8 of this report. Seep data are not appropriate for assessing ecological risks and therefore were excluded from the TZW-BERA.~~

~~The groundwater seep data set is limited and does not lend itself to the general organization of the nature and extent discussion applied to TZW and other media in this report (specifically, discussion of select analytes followed by remaining ICs and a summary). Instead, this section will present all available seep locations and data of adequate quality for use in BHHRA, presenting simple comparisons of concentration to upland groundwater and TZW, to provide context and support understanding of the groundwater seep data.~~

~~5.5.110.35.5.2.1~~ **Groundwater Seep Locations**

A seep reconnaissance survey was conducted during Round 1 of the Portland Harbor RI/FS (GSI 2003b) to support the BHHRA and ~~development of the~~ CSM. This survey documented readily identifiable groundwater seeps based on visual observations along approximately 17 miles of riverbank from RM 2 to 10.5. For the purposes of this survey, a seep was defined as groundwater discharge above the Willamette River water line as observed during the seep reconnaissance survey. This groundwater may be discharged from local shallow groundwater systems, perched groundwater, water seeping through utility backfill, or return flow from tidally influenced bank storage. Observed seeps were classified into one or more of five types:

- Seepage line at the base of embankments (nine seeps)
- Linear and point seeps at the foot of beaches (six seeps)
- Seepage through backfill surrounding outfalls (four seeps)
- Seepage of NAPL (two seeps)
- Potential seep locations identified by observation of extensive ferric hydroxide staining of bank materials (eight potential seeps).

Additionally, eight seeps were categorized as combinations of the above seep types.

~~5.5.2.2 Twelve seeps were observed at or near potential human-use areas (GSI 2003b). No additional seeps or other surface expressions of groundwater have been observed on or near a human-use beach since the seep reconnaissance survey.~~

~~5.5.110.4~~ **Groundwater Seep Water Quality Data**

~~Seep W~~water quality ~~data samples~~ have been collected at six seeps in four general areas (Figure Map 5.4-57). ~~Groundwater seep discharge rates have not been empirically~~

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~~quantified.~~ The water quality sampling efforts ~~conducted to date~~ for upland groundwater seeps include:

- City of Portland stormwater Outfalls 22B and 22C, located directly north and south of the Railroad Bridge at RM 6.89 and 6.82, respectively, are type 3 (backfill surrounding outfalls) seeps. Both Rhone Poulenc and NW Natural have collected water quality samples in Outfalls 22B and 22C to evaluate potential groundwater infiltration to the conveyance systems. The samples were analyzed for conventional parameters, metals, PCB Aroclors, PCDD/Fs, pesticides, PAHs, phthalates, SVOCs, phenols, petroleum hydrocarbons, and VOCs.
- Rhone Poulenc sampled Outfall 22B on five occasions between October 1, 1993 and September 23, 2004 and Outfall 22C four times between August 13, 2002 and September 23, 2004. Samples were collected at the end of the pipe and were analyzed for 231 individual parameters, including conventionals, PCDD/Fs, herbicides, metals, PAHs, PCB Aroclors, pesticides, petroleum hydrocarbons, phenols, phthalates, SVOCs, and VOCs. The results are Category 1 data validated to the QA2 level.
- NW Natural sampled Outfall 22C on February 24, 2005 for 89 individual parameters, including conventionals, metals, PAHs, phenols, phthalates, SVOCs, and VOCs. Data were validated to Category 2, QA1 level.
- Seeps-01, -02, and -03 are located at the Gunderson site near RM 8.5. These type 3 seeps are associated with cracked stormwater drain pipes. Each seep was sampled once in November 2004 and again in April 2005, with samples analyzed for 31 individual parameters, including conventionals, metals, PCB Aroclors, PAHs, petroleum hydrocarbons, and phthalates. Data were validated to Category 1, QA1.
- ExxonMobil sampled areas with visible sheen on sand and in pooled water along the riverbank at the ExxonMobil site under the direction of DEQ on August 13, 2004 (Kleinfelder 2004). Two composite samples were analyzed as soils for DRH, GRH, and RRH. Data were validated to the QA1 level.

A summary of the IC data collected at each of the above mentioned locations is provided in Table 5.5-2. All of the seep data collected from these locations is presented in Appendix D4 (Table D4-2).

5.5.2.2.1 Outfalls 22B and 22C

As indicated above, the City of Portland and Rhone Poulenc collected samples from Outfall 22B and Outfall 22C. In addition, NW Natural collected samples from Outfall 22 C. The analytical results for the ICs detected in these samples are summarized below.

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Total PCBs

Total PCDD/F and TCDD-TEQ

Total DDX

Total PAHs

BEHP

Total Chlordanes

Aldrin

Dieldrin

Arsenic

Chromium

Copper

Zinc

TBT Ion

5.5.2.2.2 Seep-01 through Seep-03

Of the ICs, PAHs, BEHP, and four metals (arsenic, chromium, copper and zinc) were detected above laboratory reporting limits in one or more samples collected from these three seeps. The remaining ICs for which analysis was conducted were not detected.

Total PAHs

PAH analysis was conducted for the sample collected from Seep-01 in April 2005; however, PAHs were not detected. PAHs were detected in both samples collected from Seep-02, with total PAH concentrations of 3.19 J ug/L (November 2004) and 4.53 J ug/L (April 2005). PAH analysis was not conducted for samples collected from Seep-03.

BEHP

The samples collected from Seep-01, Seep-02, and Seep-03 during both sampling events were analyzed for BEHP. BEHP was not detected in either sample collected from Seep-01. BEHP was detected at concentrations of 0.527 ug/L (November 2004) and 1.65 ug/L (April 2005) in the samples collected from Seep-02. BEHP was detected

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in the sample collected from Seep-03 in November 2004 at a concentration of 2.74 ug/L, but was not detected in the sample collected from Seep-03 in April 2005.

Arsenic

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The samples collected from Seep-01, Seep-02, and Seep-03 during both sampling events were analyzed for arsenic. Arsenic was detected in the sample collected from Seep-01 in November 2004 at a concentration of 1.15 ug/L, but was not detected in the sample collected in April 2005. Arsenic was detected at concentrations of 6.03 ug/L (November 2004) and 4.79 ug/L (April 2005) in the samples collected from Seep-02. Arsenic also was detected in the samples collected from Seep-03 at concentrations of 46.6 ug/L (November 2004) and 1.92 ug/L (April 2005).

Chromium

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The samples collected from Seep-01, Seep-02, and Seep-03 during both sampling events were analyzed for chromium. Chromium was detected in both samples collected from Seep-01 at concentrations of 2.32 ug/L (November 2004) and 2.44 ug/L (April 2005). Chromium also was detected at concentrations of 41.4 ug/L (November 2004) and 25.2 ug/L (April 2005) in the samples collected from Seep-02. Chromium was detected in the samples collected from Seep-03 at concentrations of 46.5 ug/L (November 2004) and 1.94 ug/L (April 2005).

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Copper

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The samples collected from Seep-01, Seep-02, and Seep-03 during both sampling events were analyzed for copper. Copper was detected in both samples collected from Seep-01 at concentrations of 140 ug/L (November 2004) and 32.5 ug/L (April 2005). Copper also was detected at concentrations of 373 ug/L (November 2004) and 241 ug/L (April 2005) in the samples collected from Seep-02. Copper was detected in the samples collected from Seep-03 at concentrations of 1,500 ug/L (November 2004) and 5.44 ug/L (April 2005).

Zinc

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The samples collected from Seep-01, Seep-02, and Seep-03 during both sampling events were analyzed for zinc. Zinc was detected in both samples collected from Seep-01 at concentrations of 573 ug/L (November 2004) and 215 ug/L (April 2005). Zinc also was detected at concentrations of 1,450 ug/L (November 2004) and 1,170 ug/L (April 2005) in the samples collected from Seep-02. Zinc was detected in the samples collected from Seep-03 at concentrations of 2,060 ug/L (November 2004) and 787 ug/L (April 2005).

5.5.2.2.3 Exxon Mobil

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The sampling events described above summarize all groundwater seep data collected to date; the associated data table presented in Appendix D4 (Table D4-2) focuses only on the City of Portland Outfall 22B seep location, which is the only seep relevant for use in the BHHRA based on data quality and location. Outfall 22B is located on a human-use beach (Figure 5.4-5) and has Category 1 data validated to the QA2 level.

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For this nature and extent discussion, a subset of the detected Category 1, QA2 Outfall 22B seep data was compared to nearshore upland groundwater data and TZW data from the Rhone Poulenc site (Figure 5.4-6). Because of the small number of seep, upland groundwater, and TZW samples, these data are presented as a simple comparison and should not be considered statistically significant. At Outfall 22B, detected seep concentrations of Silvex (0.14 µg/L), benzene (0.19 µg/L), and TCE (0.34 µg/L) were below the minimum concentrations found in upland groundwater and in TZW. The measured concentration of 1,2-DCB at Outfall 22B (0.864 µg/L) falls within the lower end of the range for upland groundwater and TZW.

5.5.111 Summary of Indicator Chemicals in TZW and Seeps

The following subsections present a brief summary of the findings for TZW and groundwater seeps.

5.5.111.1 Transition Zone Water Summary

The preceding discussions present the observed distribution and patterns of ICs in TZW. The TZW data set was generated for the purposes of assessing TZW offshore of upland groundwater plumes with likely or known complete pathways to the river; therefore, the data set does not cover all areas where TZW may be affected by unknown plumes or TZW quality impacted by contaminated sediments. Specifically, the data set is focused on the offshore area of nine sites, identified as high-priority, Category A upland groundwater sites due to a confirmed or reasonable likelihood for discharge of upland groundwater COIs to Portland Harbor. Consideration of pore water chemistry affected by in-river sediment contamination is evaluated in Section 6 through equilibrium partitioning calculations based on the large data set of sediment concentrations.

The observed distribution of TZW chemicals could not be adequately described focusing exclusively on the bounding ICs (total PCBs, total PCDD/Fs, total DDX, and total PAHs) because these chemicals were often not part of the focus of the upland site plume-defined analyte lists. Therefore, the TZW nature and extent presentation briefly addresses all TZW ICs, as opposed to focusing on chemicals also included as CSM ICs. Note that PCBs were not sampled in TZW, and only two TZW sampling locations were analyzed for PCDD/Fs; these chemicals are not included in the TZW nature and extent discussion.

DDX was measured in TZW at ten locations offshore of the former Acid Plant area of the Arkema site, as well as at one location offshore of the adjacent Rhone Poulenc site.

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The highest concentrations were observed in unfiltered samples collected in both shallow (0 to 38 cm bml) and deep (90 to 150 cm bml) TZW samples offshore of the former Acid Plant area. Review of the filtered and unfiltered results indicates that DDx is present on solids. Further, concentrations in unfiltered samples are generally greater in deep than shallow TZW samples. These results with filtration and depth were not apparent in the limited data collected at the single sample location offshore of the Rhone-Poulenc site.

PAHs were sampled at six of the TZW sites (Kinder Morgan, ARCO, ExxonMobil, Gasco, Siltronic, and Willbridge Terminal). Total PAH concentrations were found to be highest offshore of the Gasco and Siltronic sites. Total HPAH, total cPAH, and BAP results showed similar distribution and filtration patterns. Because LPAHs tend to comprise the majority of the total PAH concentrations, LPAH and naphthalene results generally followed the distribution patterns apparent for total PAHs. Filtration was observed to decrease the total PAH concentration slightly, with greater effects on the more hydrophobic PAHs, as expected. Review of the fractional composition of the 17 individual chemicals that compose total PAHs shows a clear pattern of high naphthalene concentrations associated with high total PAH concentrations offshore of the Gasco and Siltronic sites.

TPH was sampled at six of the TZW sites (Kinder Morgan, ARCO, ExxonMobil, Gasco, Siltronic, and Willbridge Terminal). The highest concentrations of TPH in TZW were observed offshore of the Gasco and Siltronic sites, with the highest individual result measured offshore of the Gasco site. The complex mixture nature of the analyte TPH, however, confounded detailed interpretation of results. Overall, filtration was observed to decrease TPH concentration; however, it is unclear whether this effect is related to loss of volatiles during filtration or loss of more hydrophobic portions of the TPH mixture, with composition varying in inconsistent ways across filtration pairs. Review of the fractional components (DRH, RRH, and GRH) showed a pattern of TPH composition shift toward GRHs offshore of a portion of the Siltronic site, but did not provide useful insights elsewhere.

Cyanide, Silvex, and perchlorate were detected offshore of the sites where they were sampled in areas that also showed detections of other upland COIs on the TZW analyte list for the sites. The highest detections of Silvex were observed offshore of the Rhone Poulenc site in an area thought to be an offshore discharge area for upland groundwater. Total cyanide was detected offshore of the Gasco and Siltronic sites. Perchlorate was observed offshore of the Arkema site former Chlorate Plant area.

The TZW IC list includes eight metals: arsenic, barium, cadmium, copper, lead, manganese, nickel, and zinc. These were sampled offshore of all nine TZW study sites. Filtration significantly and consistently reduced TZW sample concentrations for cadmium, copper, lead, nickel, and zinc, suggesting that much of the observed total concentration for these metals was associated with $>0.45\text{ }\mu\text{m}$ particles. Differences with filtration were not as pronounced for arsenic, barium, and manganese. Shallow

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versus deep TZW results did not show consistent trends for any of the metals. The spatial distribution of metals likely reflects some combination of upland groundwater transport, local sediment redox conditions, and sediment contamination, varying by site and metal. Detailed geochemical analysis of select metals concentrations in TZW is provided in Appendix C2.

The TZW IC list includes nine chlorinated VOCs (MCB; chloroethane; 1,2-DCA; 1,1,2-TCA; vinyl chloride; cis-1,2-DCE; TCE; chloroform; and methylene chloride) and one chlorinated SVOC (1,2-DCB). These chemicals were sampled at all nine TZW study sites. In summary, the chlorinated VOCs and 1,2-DCB show spatial distribution patterns that appear to reflect common groundwater pathways and degradation chains. Specifically, the highest concentrations of TCE, cis-1,2-DCE, and vinyl chloride are located offshore of the Siltronic site and the former Acid Plant area of the Arkema site. Likewise, the highest concentrations of 1,1,2-TCA, 1,2-DCA, and chloroethane are generally located offshore of the former Acid Plant area of the Arkema site and the Gunderson site. Further, the majority of detected results for chloroform and methylene chloride are also generally located offshore of the Arkema site. Finally, the highest concentrations of 1,2-DCB and MCB are generally located offshore of the former Acid Plant area of the Arkema site and the Rhone Poulenc site.

The TZW IC list includes two non-chlorinated VOCs, 1,2,4-trimethylbenzene and carbon disulfide. Carbon disulfide was sampled at all nine TZW study sites, but 1,2,4-trimethylbenzene was sampled offshore of the Siltronic site only. The highest concentrations of carbon disulfide were observed offshore of the Gasco site. These high concentrations were generally observed in areas of other elevated VOCs offshore of this site.

BTEX was analyzed in TZW samples from all nine study sites. The highest values were consistently observed offshore of the Gasco and Siltronic sites, with one high value also observed offshore of Arkema.

5.5.111.2 Groundwater Seeps Summary

The groundwater seep data are limited and do not allow for definitive conclusions. Only one seep, Outfall 22B (at the Rhone Poulenc site), is relevant for use in the BHHRA. At this location, groundwater infiltrates into the outfall pipe, which subsequently discharges to a beach. The beach where Outfall 22B discharges was identified as a potential transient use area, so exposure to the groundwater seep in that beach by transients is considered a potentially complete pathway. For most analytes evaluated, Outfall 22B concentrations were near or below detection limits and were well below nearby upland groundwater and TZW concentrations.